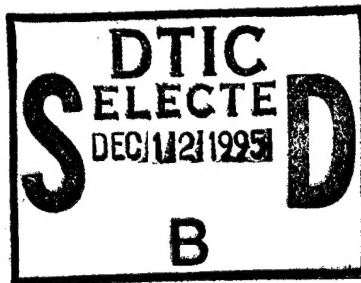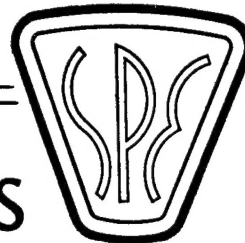# TECHNICAL PAPERS

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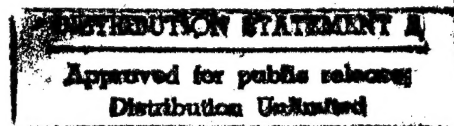
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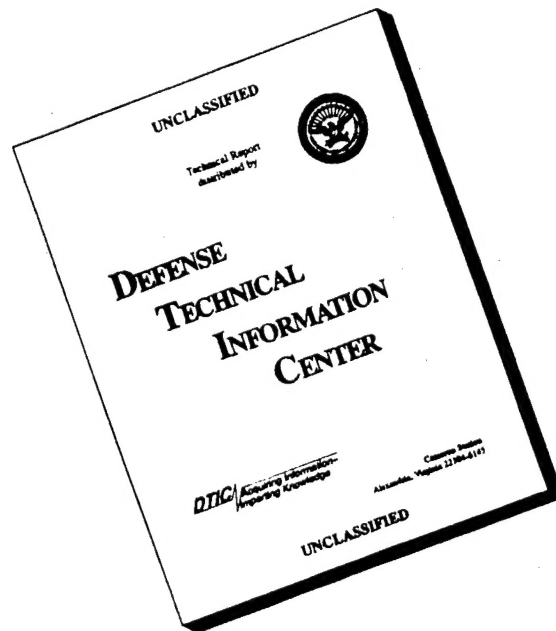
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Regional Technical Conference

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April 28, 1966

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VINYL DISPERSION COATINGS IN THE ORGANIC FINISHES INDUSTRY

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and

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We thought that you would be interested in learning at this Conference what has been happening in the field of vinyl dispersion coatings in the organic finishes industry during the past few years. This paper will not review the older or more conventional uses of dispersion coatings, but will report on some of the newer uses in the organic finishes or paint industry.

At this time, most dispersion coatings available on the market are based largely on the polyvinyl-chloride homopolymer type of resin. While other types of dispersion coatings, such as those based on polyvinyl fluoride and polyvinylidene fluoride are beginning to appear on the market place, major reference will be made to the polyvinyl chloride type of dispersion coatings which are finding important new applications in industrial finishes today because of their economy and excellent performance characteristics.

In 1944, a real break-through was made by Quarles and Powell of the Union Carbide Plastics Co., when they developed a new way of taking advantage of the good properties of high molecular weight vinyl chloride resins by discovering what is now known as the "dispersion technique". The dispersion coatings made by the "dispersion technique" and the improvements thereon will be the subject of our discussion in this paper.

Dispersion coatings, also known as organosols and plastisols, are much more recent than the conventional solution vinyl coatings which performed so well for the organic coatings industry over the past twenty-odd years, and which are still used today in good quantity. These solution vinyl resin coatings are based on copolymers of vinyl chloride and vinyl acetate and are of relatively low molecular weight. Polymers containing third components have also been introduced and are to provide the industry with vinyl polymers which are carboxyl (-COOH), hydroxyl (-OH) or otherwise terminated for the attainment of special properties.

It has long been known that the higher molecular weight vinyl resins produced films which gave the best toughness and resistance properties. The resultant

coatings, however, had poor adhesion to metal substrates, gave very low solids when dissolved in even the strongest solvents and exhibited poor flow properties as well. By not dissolving this resin, but dispersing it suitably, the new family of coating materials which we shall discuss today was born - dispersion coatings.

A vinyl dispersion is a suspension of colloidal size particles in an organic medium which is not capable of dissolving the resin at room temperature, but which exerts some solvating or peptizing effect on the polymer particles. When the organic medium contains volatile solvent(s) the mixture is called an organosol. Mixtures which do not contain appreciable amounts of volatile thinner(s) are referred to as plastisols. Organosol dispersions normally contain 40-80% solids whereas plastisols contain 90-100% solids.

The resin particle diameter range varies from 0.1 to 1.0 microns. Relative viscosity is in the range 2.50 to 3.0 for the higher molecular weight resins and 2.05 to 2.4 for the lower molecular weight materials. Relative viscosity (ηr), also referred to as viscosity ratio, is defined as the ratio of the viscosity of a 1% resin solution in cyclohexanone at $25^{\circ}C$, to the viscosity of pure cyclohexanone at $25^{\circ}C$.

In general, dispersion coatings are composed of the ingredients shown in Table I.

The liquid phase, i.e. solvents, diluents, and plasticizers of the dispersion system perform multiple functions such as wetting aids, dispersing media, viscosity depressants (thinner) and stabilizers, and fusion aids.

Because of this multiple role, these liquid components must be meticulously selected to achieve a dispersion system with proper application and coalescing properties. Not only must they be perfectly balanced for good flow properties to prevent flocculation or over-solvation and even gellation of the dispersion resin, but consideration must be also given to the requirements of and interactions with the other formula ingredients, such as the pigment, resin and other modifying materials.

Figure 1 reveals graphically in the case of a simple organosol what the microscope might show if the solvent system were properly balanced, flocculated (excess diluent), and oversolvated (excess dispersant). In the chart on Figure 1, we see that the viscosity rises rapidly with imperfectly balanced solvents, either undersolvated (flocculated) or oversolvated.

In Figure 1, the term "diluent", refers to hydrocarbons such as Mineral Spirits or the widely known #100 or #150 solvent. The term "dispersant" refers to polar solvents such as diisobutyl ketone, methyl isobutyl ketone, isophorone, cyclohexanone, dimethyl formamide or methyl amyl acetate.

One of the defects noticeable in an organosol film with inadequate solvent balance is called "mud-cracking". The organosols are prone to this condition because they inherently tend to release solvents very rapidly. In a deposited film, a too rapid loss of solvent results in volume shrinkage and hence causes "mud-cracking". This condition can be avoided by combining a fast cure rate (to quickly coalesce or fuse the tiny resin particles) with a "slow" solvent system to keep the film "mobile" for as long as is necessary to obtain optimum film properties.

In some specially developed organosol coating systems, it has been

practically impossible to design solvent systems which would produce good flow, aid in proper fuse-out of the film and still be viscosity-stable on storage. Such coating materials are sold as two-package systems. The organosol component contains a balanced solvent system for the ingredients contained therein, yielding a storage-stable liquid which may be clear or pigmented. The catalyst component, which may contain the modifying resins or cross-linking agents also utilizes solvents which are properly balanced for this component and it, too, forms a storage-stable liquid, clear or pigmented, as the case may be. The organosol and catalyst components are usually mixed equal parts by volume to form a coating with the desired end properties. In approximately six hours (depending on specific composition, ambient temperature and humidity), oversolvation may start and viscosity begin to rise. In such a case, fresh "equal parts" mixture is added, and the blend may normally be used with complete satisfaction. In commercial practice, the make-up or replenishing coating material effectively eliminates any practical concern regarding viscosity rise. Any catalyzed mixture held over a weekend, for example, is merely checked for fluidity and added to a fresh "equal parts" mixture.

When storing dispersion systems, one should recognize that the dispersants or polar solvents are more powerful in their action at higher temperatures and hence organosol materials should not be stored in the hot sun or next to radiators where the coating temperature will rise to higher than 120°F or oversolvation may occur. Also, since solvent power falls off with the reduction of ambient temperatures, undersolvation and possibly flocculation may occur if organosols are stored outside for long periods during the winter in cold areas. Never heat up dispersion coatings rapidly with devices such as immersion heaters or oversolvation and even gellation can occur.

Dispersion resins can be applied by a variety of methods including spray, knife, roller, dip and extrusion. While spraying techniques are mostly reserved for organosols and extrusion procedures for plastisols, the other methods are common to both type systems. The choice of method of application or dispersion systems (organosol or plastisol) is dictated by film thickness requirements, available application techniques (i.e.,spray, extrusion) and/or processing equipment (i.e., shear mixers or roller mills) substrates, and of course, product performance.

It is interesting to note that, due to the puffy or thixotropic nature of dispersion coatings, these materials can be applied at much higher than normal viscosities. The shear forces exerted during recirculation and in the coating roller nip of a roller coater; or during spraying; or during extrusion are effective in reducing the actual coating viscosity of these materials. In addition, flow is assisted by the normal coalescence or fusion of the resin particles in the baking oven.

All dispersion coatings must be properly baked or fused in order to coalesce the tiny dispersed resin particles into a continuous, tough, and flexible film. Depending on formulation and dwell time, the required fusing temperatures (based on actual metal temperatures) varies from 300-525°F. The preferred cycle for sheet bakes is ten minutes in the 350-525°F range. In moving web application, i.e., coil or strip coating, a cure cycle of sixty seconds or less at about 525°F yields good results. These cited examples, of course, are for vinyl chloride dispersion systems. Fluorinated dispersion coatings require substantially higher temperatures, (approximately 550-600°F) for proper film formation.

Since fusion of the dispersed particles is the major objective in the curing procedure, the baking cycle for a given application depends upon how quickly the wet film reaches fusing temperature. When this critical temperature is reached, the tiny, partially-solvated particles quickly coalesce into a homogeneous and

continuous film. Figures 2, 3 and 4 are electron micrographs showing the various stages of film coalescence.

Problems of thermal degradation will occur if the coating is subjected to temperatures in excess of 500°F for vinyl chloride dispersion; in excess of 600°F for vinyl or vinylidene fluoride dispersions for prolonged periods.

In the instances of vinyl chloride dispersion, the rate of thermal decomposition is accelerated in the presence of iron; and such situations occur, for example, when microscopically exposed tin plate is subjected to extreme temperature for only a few seconds. The resultant film is discolored black. Discoloration of this type can also mean that the oven has been set too high or developed a hot spot or similar difficulty. To deter these thermal effects, 1/2-5pph of a stabilizer is admixed in the dispersion composition. Effective stabilizers include, metallic soaps, organic tin and cadmium salts, and epoxide resins.

Vinyl and vinylidene fluoride systems, although more thermally stable than their vinyl chloride cousins, undergo thermal decomposition at relatively high temperatures (>600°F). The process is greatly accelerated in the presence of glass or silica and these materials are to be avoided in formulating these systems. Copper, aluminum and iron show no catalytic degradation effects; although, surprisingly, rutile titanium dioxide shows a tendency to discolor the vinylidene fluoride systems and discoloration becomes more pronounced with increasing pigment concentrations. Effective stabilizer products for these dispersion resins are calcium-zinc complexes or pentaerythritol in combination with an anti-oxidant.

We have found that film integrity, gloss, flexibility and process or hot water resistance are materially affected by the baking cycles used. In pratice, the fusing cycle must be especially established for each application. In general, optimum results are obtained when the coated metal is exposed to relatively high temperatures in the first oven zone. By doing this, the solvents in the dispersion composition have an opportunity to help solvate the dispersion resin before they are evaporated. Of course, care must be taken to adjust the temperatures in the first oven zones so that no blistering or pin holes occur.

Based on practical and theoretical consideration with PVC dispersion coatings, we found that 335°F is the minimum metal temperature at which the polyvinyl chloride dispersion should be fused for good results. A recommended sheet coating schedule, for example, would be 340°F to 365°F for six to ten minutes. A representative coil bake would be 60 seconds at 500°F for 0.6 mil film. Properly cured films, thus baked achieve tensile strengths of 8,000 to 10,000 lbs. per square inch. Elongation is approximately 300%.

Similar curing considerations apply to the fluoropolymers. However, these coatings require considerably more energy to properly coalesce the film. Metal temperatures of 475°F, approximately 100 F above those used for the vinyl chloride systems, are demanded. A representative coil bake, for these resins, for example, would be 425 to 475°F for 30 to 45 seconds.

Table II presents the results obtained when pigmented vinyl chloride dispersion films applied at 30 mg/4 in.^{2} to 0.010" chromate-phosphate treated 5052 alloy are cured at different temperatures and then subjected to 60 minutes steam sterilization at 15 lbs/in.^{2} at 250°F.

It is apparent from this example that optimum film properties are obtained only if adequate cure cycles are used.

Dispersion type coatings have the following advantages for the organic finishes industry as shown in Table III.

Dispersion films are generally less expensive, more durable, inert, chemically resistant and perform better than ordinary or solution vinyl films. The lower molecular weight of the solution resins and/or modifications with other monomers are major causes for these differences. The solution resins do, however, have important advantages such as high gloss, low temperature film formulation and good adhesion to metal substrates. They are often added to dispersion coatings to take advantage of these properties, in many instances, without diluting the outstanding properties of the dispersion resin.

Because of their excellent chemical resistance properties, dispersion resins have qualified for usage in such diverse areas as liquid detergents, and waxes, artist clay, water base paints and cleaners and shellac. It is interesting, for example, that one of the first commercial utilizations of dispersion coatings in the metal-litho field was for the hard-to-hold liquid detergents which made their appearance on the American market about eight years ago. Prior to this time, the dispersion resins were used to contain strong liquid detergents, waxes and liquid cleaners; however, these earlier systems consisted of a size and a dispersion top-coat because at that time the dispersion coatings alone did not have adequate adhesion to tin plate and other metal substrates.

Shortly after vinyl chloride dispersion coatings were developed, it was apparent that these compositions were exceptionally suited for use as container and closure coatings for food and beverage products. They are effective in this application because of non-toxicity, lack of odor and taste, and the ability to take a deep draw in the making of aluminum cans. Since their introduction in this market, many proprietary coatings have been developed and these have met the extractability and other safety requirements of the Food and Drug Administration. A partial list of food products used in contact with vinyl dispersion linings are shown in Table IV. Typical containers used to hold these products are shown in Figure 5. Figures 6 and 7 demonstrate the deep draw abilities of these coatings.

During the past decade, coating research laboratories have been actively developing durable and weatherable coating compositions based upon vinyl dispersion resins and other newer synthetic resins. As a result of this work, a new "breed" of outstanding coatings materials have been created and many unique compositions are now used in the industrial and residential building products field.

Among those most suitable in this application, coatings containing silicone copolymers, fluorocarbon dispersion and vinyl chloride dispersion resins, have been found, in general, to possess good to excellent weatherability and inertness to atmospheric chemical polutants. The vinyl solution and acrylics have, in recent years, been found somewhat wanting in resistance to chalk and bodying on extensive weathering exposure.

As shown in Table V, compositions prepared with silicone copolymers and fluorocarbon polymers perhaps perform the best on weathering, and although somewhat expensive, are in demand as "premium" coatings by high quality and/or institutional buyers. These expensive and durable coatings are primarily used in industrial, maintenance, residential siding, hospital, school and business building applications. Projections based upon extensive weatherometer aging, outside exposure and other performance data indicate that substrates coated with these materials have excellent protection against weathering and chemical decomposition for periods up to 20 years. As a result of these tests, buildings coated with these materials may carry a guarantee against chalking and discoloration. Vinyl organosol coatings represent a good value for these same end uses, being considerably less

-5-

expensive but weathering reasonably well.

At several points during this presentation reference was made to the weatherability properties of coatings and it is appropriate at this point to define this property and elaborate on some widely used evaluating techniques.

Weatherability refers to the physical condition of a coating after extensive exposure to a variety of natural climatic conditions; or exposure to equipment which is designed to simulate the effects of outside exposure.

In the instance of exterior exposure, coated panels are exposed at Arizona and Florida locations for extended periods, both at 45° So. and horizontal. At six (6) month intervals (usually) the condition of each coating is evaluated with regard to chalking, checking, cracking, crazing, peeling, color stability and adhesion. Florida and Arizona locations are commonly used as test sites because they are widely accepted as being representative of severe exposure conditions within this country. The results obtained at these locations reflect a vigorous performance evaluation.

The basic problem with outside exposure techniques is the long periods required to obtain test results. To obtain data more rapidly, equipment has been developed which artificially produces a natural-type environment.

Many investigators have reported on this equipment and the correlation obtained with outside exposure. The consensus is that this equipment offers a rapid and reproducible technique for rating the performance of materials. There is much controversy, at present, regarding the interpretation of test data as it relates to natural exposure time.

For our purposes, we have found that the Atlas Dew Point Weather-Ometer is an excellent unit for obtaining accelerated exposure information, for comparing and/or predicting the weathering performance, especially chalking of coatings.

In operation, the unit is programmed such that:

1. All exposures are run at 100% relative humidity.

2. The radiation sequence is composed of a 60-minute light, 60-minute dark cycle, and

3. A cold spray $(40-42^{\circ}F)$ is applied to the back of the panels during the dark cycle.

It is this combined sequence of events which gives controlled reproducible results.

In comparing Dew-Point Weather-Ometer exposure results of vinyl chloride organosol coatings with those of identical panels exposed in Florida, we have found that 75-100 hours' exposure correlates quite well to "two (2) summers" exposure in the natural climate.

Although not as unique as their other contemporary cousins, coatings containing vinyl chloride dispersion, vinyl chloride solution and acrylic resins offer adequate performance at moderate cost and hence are used in great abundance in about every facet of the organic finishes industry. Within the group, of course, performance differences do exist and Tables VI and VII and Figure 8 reflect the decree that is to be expected.

From this comparison, it is interesting to note that the vinyl dispersion systems offer more than adequate performance at a low cost – a factor which has encouraged usage of this material in the residential building products field; particularly in roof-siding and related applications. Figures 9, 10 and 11 are examples in which these dispersion systems have successfully performed in the building products field. Other applications include organic finishes for business machines, instrument panels, electronic devices and television cabinets.

Through American-associated companies abroad, dispersion coatings, primarily the polyvinyl chloride type, are being used in Europe, Latin America, Australia and Japan in applications typical of those shown in Table VIII. It is also noteworthy that these coatings are preferred for aerosol cans made with aluminum bodies and tinplate ends because the dispersion film, being excellent as an insulator, eliminates bi-metallic couples and destructive electrolytic cell effects which might otherwise occur.

From the preceding discussion, it is apparent that (the use of dispersion coatings in the organic finishes industry has only "scratched" the surface. New improvements in the quality, variety and uniformity of vinyl homopolymers, increased "know-how" of coatings manufacturers, new dispersion techniques and new markets are factors which will contribute to continued growth in the years to come.] For example, the authors are presently involved in studies of new dispersion techniques which result in dispersion films having a Gardner 60° gloss in excess of 90° and which will enable the usage of dispersion coatings in areas hitherto disallowed because of gloss limitation. We are also aware of [intensive dispersion coatings research programs in the coil-coatings, electronics, and building product field, results of which will undoubtedly lead to increased consumption of these dispersion coatings in industry.]
are being conducted

ACKNOWLEDGMENT

The illustrations showing the electron micrographs of organosol films and the solvent balance curves are used with the kind permission of the Union Carbide Corp.

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TABLE I

GENERAL COMPOSITION OF DISPERSION COATINGS

Dispersion Resin(s)
Pigments
Plasticizers
Diluents and Solvents
Stabilizers and Cross-Linking Agents
Modifying Resins

Acrylic   Oleoresinous
Alkyd   Phenolic
Amino   Polyester
Epoxy   Silicone
Hydrocarbon   Vinyl Copolymers
  (incl. Polybutadiene)   Other
Ketone

TABLE II

Cure Cycle, 60 sec. @ °F.	"Scotch Tape" Adhesion Test	Blistering
400	Poor-30% area remaining	Moderate
425	Fair-85% area remaining	Slight
450	O.K.	None
475	O.K.	None
500	O.K.	None

TABLE III

ADVANTAGES OF DISPERSION COATINGS FOR ORGANIC FINISHES

Toughness . . . . Excellent
Impact Resistance . . . . Very High
Tensile Strength . . . . Very High
Chemical Resistance . . . . Unaffected by dilute and concentrated acids and alkalis.

Resistant to organic solvents, alcohols, greases and aliphatic hydrocarbons. Inert to water and aqueous salt solutions.

Abrasion Resistance . . . . Excellent
Water Absorption . . . . Very Low
Moisture Vapor Transmission . . . . Very Low Rate
    Flammability . . . . Non-flammable
    Toxicity . . . . Odorless, tasteless and non-toxic
    Heat Sealing Properties . . . . . Good
    Weatherability. . . . . Good-Excellent
    Stability . . . . Good-Excellent
Adhesion (unmodified). . . . . Poor
Adhesion (modified). . . . . Poor-Excellent

TABLE IV

FOOD PRODUCTS USED IN CONTACT WITH DISPERSION LININGS

Applesauce	Liver Pastes
Artichoke Hearts	Mincemeat
Asparagus	Mushroom Sauce
Baby Foods	Olives
Beef Stew	Pickled Beets
Beer	Pickled Fruits
Boiled Onions	Pickles
Boned Chicken	Pimento
Candied Fruits	Potato Salad
Carbonated Beverages	Potted Meats
Cheese Spreads	Preserves
Chili	Red Cabbage
Cocktail Frankfurters	Salad Dressing
Cooked Fruits	Sauerkraut
Corned Beef Hash	Tomato Juice
Cranberry Relish	Tuna Fish
Jellies	Vienna Sausage

TABLE V

GENERAL PERFORMANCE COMPARISON

1000 Hours' Exposure	Silicone Polyester	Fluorocarbon Resin	Vinyl Chloride Dispersion
Atlas Weather-Ometer	Excellent	Excellent	Good
Relative Humidity Resistance (100% R.H. @ 100°F)	Excellent	Excellent	Very Good
5% Salt Spray (ASTM D117-S7T)	Excellent	Excellent	Very Good
Water Soak	Excellent	Excellent	Very Good
Cost/sq.ft.-1.0 mil film (Range)	.95-1.75¢	5.0-8.0¢	0.75-0.9¢

TABLE VI

GENERAL PERFORMANCE COMPARISON

1000 Hours' Exposure	Vinyl Chloride Dispersion	Vinyl Solution	Modified Acrylic
Atlas Weather-Ometer	Good	Fair-Good	Fair-Good
Relative Humidity Resistance (100% R.H. @ 100°F)	Very Good	Good	Very Good
5% Salt Spray (AST D117-S7T)	Very Good	Good	Fair-Good
Water Soak (77°F)	Good	Fair-Good	Good

12 Months South Florida 45° South			
Resistance to Dirt Retention	Good	Good	Good-Very Good
Resistance to Chalking	Excellent	Very Good	Very Good

TABLE VII

GENERAL PERFORMANCE COMPARISON

		Vinyl Chloride Dispersion	Vinyl Solution	Modified Acrylic
Film Corrosion (ASTM B287-61)		None	None	None
Film Adhesion (Cross-Hatch)		Excellent	Fair-Good	Good
Flexibility				
Conical Mandrel		Excellent	Excellent	Good
28 mm Screw Cap		Excellent	Excellent	Fair
Gardner Impact (in.lbs.)				
Unexposed		Very Good	Fair	Good
Water Soaked	(High Gloss)	Very Good	Fair	Good
C	(Low Gloss)	Good		
Cass Test	(High Gloss)	Very Good	Fair	Fair
	(Low Gloss)	Fair		
Tabor Abrasion	(High Gloss)	.0157	.0112	.0280
(gms loss/200 cycles- CS-10 Wheel - 1000 gms weight)	(Low Gloss)	.0061		
Pencil Hardness	(High Gloss)	2H		
	(Low Gloss)	4H	3H	4H
Cost/ft.^{2} -1.0 mil film (Range)		0.75-0.9¢	0.9-1.2¢	0.65-0.85¢

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TABLE VIII

END USES FOR VINYL DISPERSION COATINGS ABROAD - 1965

CONTAINER INTERIORS

Aerosol Cans
Beer Can Ends
Beer Crowns
Deep-Drawn Food Cans
Detergent Cans
Lap-Seamed Soldered Cans (Large size for
  gherkins and other acid products)
Spray Coating for the Interior of Aluminum-
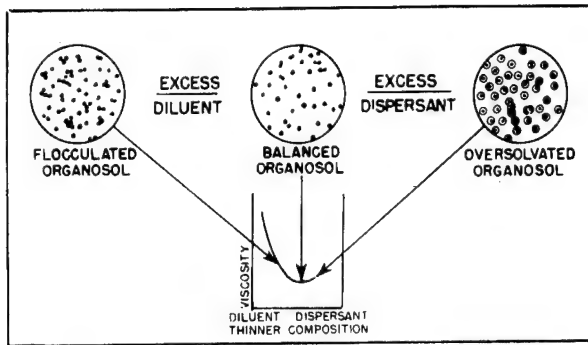 drawn Aerosol Containers

FIGURE 1: Organosol Formulating Diagram
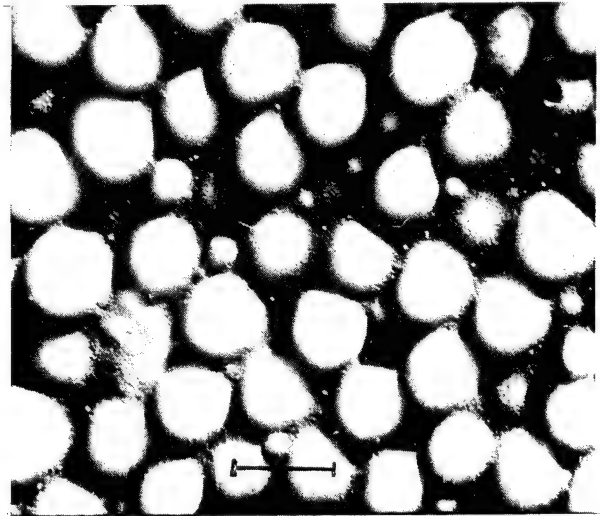
FIGURE 2: Unfused Organosol Film
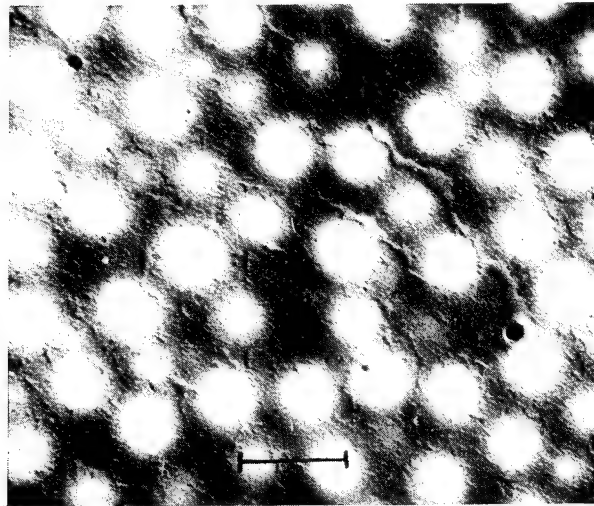
FIGURE 3: Partially Fused Organosol Film
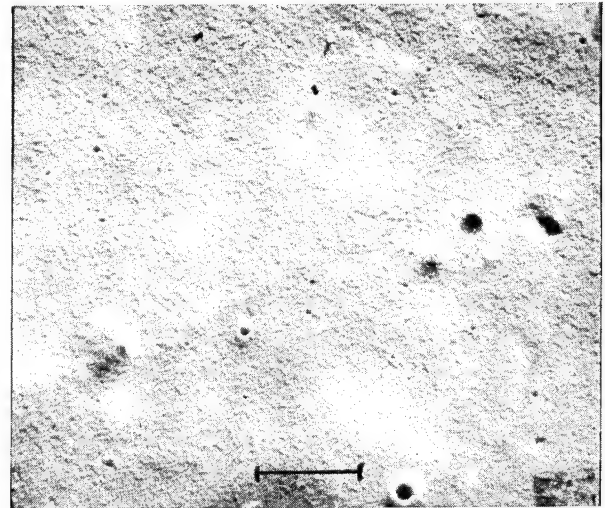
FIGURE 4: Complete Fused Organosol Film

FIGURE 5: Typical Food Container Applications
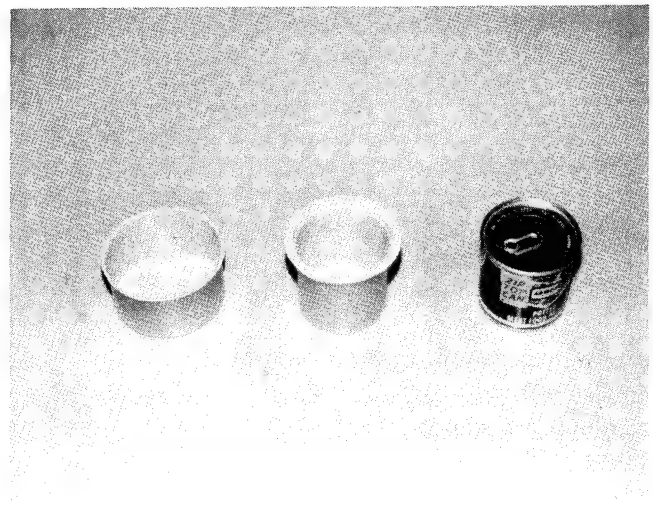
FIGURE 6: Deep-Draw Stages of Container Manufacturing
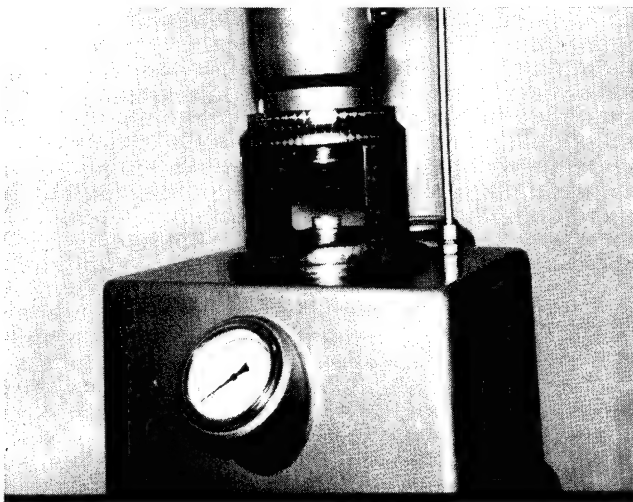
FIGURE 7: Laboratory Equipment Used To Evaluate Deep Draw Properties

Solution Vinyl Siding Coating South Florida Exposure 12 Months   Vinyl Organosol Siding Coating South Florida Exposure 12 months   Acrylic Siding Enamel South Florida Exposure 12 months

FIGURE 8: Chalking Tendencies of Vinyl Chloride Dispersion, Vinyl Chloride Solution and Acrylic Coating.

FIGURE 9: Dispersion Coatings in Residential Siding Application

FIGURE 10: Dispersion Coatings in Industrial Siding Application

FIGURE 11: Dispersion Coatings in Roof-Deck Application

PIGMENT COLORS FOR VINYL COATINGS

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Vinyl resins are well known for their many excellent properties and versatility in formulation. This makes it possible to "tailor-Make" a vinyl coating to satisfy specific needs, e.g., long term durability, resistance to any of a wide variety of chemical environments, adhesion to various surfaces, and films of desired strength, flexibility, softness or abrasion characteristics.

[Pigments are but one of many ingredients usually found in a vinyl formula. Although used primarily for decoration or opacification, they present to the formulator a completely new set of properties which must be evaluated in terms of their desirability and effect on the basic formula. Accordingly, close attention to pigment selection is necessary for optimum formulation.
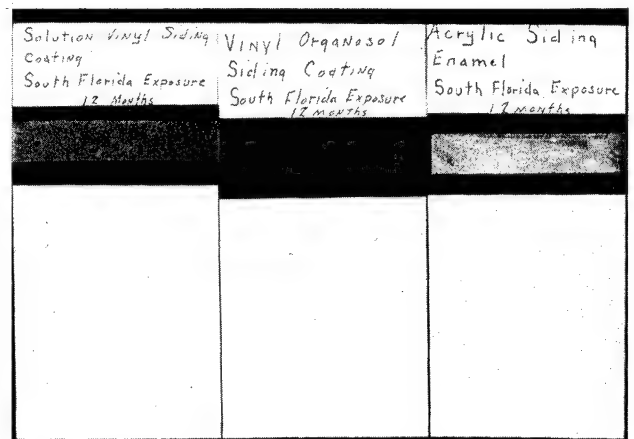
This discussion is concerned with performance of pigments in vinyl solution, plastisol and organosol coatings.] These coatings find use in many different industries, and terminology and practices vary considerably among them; accordingly, before discussing specific pigments some insight into the significance of the more important pigment properties is needed.

PIGMENT PROPERTIES

Dispersion is measured by the degree to which a pigment is reduced to an acceptable minimum particle size and maintained in that state. Dispersion to the ultimate working unit (primary particle) is rarely achieved, but dispersion must be adequate to satisfy the economic and property requirements of the coating. This may mean simply a reduction of aggregate fineness to a level that will eliminate visible specks or permit attainment of desired gloss. However, further dispersion will frequently yield greater color value and economy; this is particularly true of the higher priced organic pigments which usually develop tinting strength more slowly than fineness. Still further or more rigorous dispersion may be needed to eliminate haze and milkiness which interfere with maximum two-tone effects in metallics. Inadequate dispersion can produce bronzing and crocking.

In fluid systems, pigments may flocculate, particularly in the presence of the highly polar solvents commonly used in solution systems, thus tending to nullify the results of a good dispersion process. This can frequently be corrected or controlled through reformulation using an effective anti-flocculating agent, flocculation resistant pigment or different solvents.

Dispersion by ball milling is common practice, preferably in equipment which

avoids iron contamination. A better quality dispersion can frequently be obtained by predispersing the pigment in plasticizer on a sand or roller mill;[1] in fact, predispersion is necessary with some plastisol and organosol formulations to avoid subsequent package stability problems. Some pigments can be suitably predispersed in the Cowles, Kady, Hockmeyer or other high speed mills. However, the expensive 2-roll chip dispersion process may be needed to get high transparency desired for metallics.

Durability refers to ability to retain original appearance and film properties during exposure, i.e., ability to resist color fade, chalk fade, spotting, bronzing, checking, cracking, dirt collection, spewing, loss of gloss or change in physical properties. Opacity to ultraviolet as well as visible light must be considered in coatings intended for long term outdoor exposure; this may influence pigment loading as well as selection of a particular color.

Some coatings need only show satisfactory durability under glass or in accelerated weathering devices to be acceptable. Caution must be exercised, however, in using results obtained under these artificial conditions to predict performance outdoors; this is particularly uncertain when comparing pigments of different chemical type.[2]

Apparent pigment failure from exposure can sometimes be traced to factors other than light. The pigment may be more sensitive to moisture or atmospheric contaminants than to light, or it may slowly react with other formula ingredients. The coating itself may undergo chemical or physical changes during exposure causing separation or incompatibility of the ingredients, spewing of a liquid component, chalking of a filler, neutralization of a stabilizer, yellowing or embrittlement of the film. The greater heat absorption of dark colors may accelerate these effects and lead to early failure.

Heat stability is resistance to change in color or other properties as a result of heat encountered in either processing or end-use application. Some limitations are imposed by the vinyl resin itself, but some pigments have difficulty withstanding even short periods at common resin-fusing temperatures. Both temperature and time must be considered; recycling, heat sealing, chip dispersion, calendering and embossing all add to the accumulation of "heat history". Heat stability of a pigment frequently varies with concentration. High processing temperatures may also increase solubility or reactivity of the pigment with other formula ingredients and cause bleed, migration and viscosity changes, and other undesirable effects.

Bleed, migration, crocking, blooming and bronzing are terms often used loosely to describe the same phenomenon, i.e., the appearance of dry pigment on the film surface. In this discussion, bleed refers to inherent solubility of the pigment in one or more formula ingredients, and migration refers to its physical movement through the coating, regardless of the mechanism by which it occurs. A bleeding type pigment will migrate to the film surface, or into adjoining coatings, in an attempt to reach solution equilibrium. However, a non-bleeding pigment can also migrate as a result of physical movement of other ingredients such as occurs during spewing of a plasticizer or lubricant, or evaporation of a volatile component.

Pigments differ in solubility or bleed characteristics because of their differences in chemical structure. Some are more soluble in a plasticizer at high temperature than in so-called "strong" solvents; hence, these may show greater bleed in a fused plastisol than in an air dry solution coating. The bleed of borderline pigments can frequently be controlled by judicious selection of

plasticizers, thinners or processing conditions.

Crocking, blooming and bronzing are used interchangeably to describe the presence on the film surface of pigment which can easily be rubbed off. This may result from migration and/or bleed, inadequate pigment dispersion, abrasion or deterioration of the film surface (e.g., through exposure), high pigment loading, inadequate fusing or improper application. Bronzing more specifically describes an irridescent metallic luster produced by a film of dry pigment on a glossy surface. This is primarily a problem with dark organic colors and is attributed to simultaneous metallic and dielectric reflection of light.[3]

Blooming should not be confused with blushing which occurs in solution systems when fast evaporation of solvents cools the film below the dew point of the surrounding atmosphere and allows moisture to condense and produce a whitish discoloration on the film surface.

Plate-out describes the tendency of a pigment or other ingredient to adhere to metal surfaces such as calender and embossing rolls during processing. This may leave a loose deposit of pigment on the film surface and cause crocking or bronzing. Although inherent with some pigments, plate-out can often be controlled through improved dispersion, increased lubricant level, and change in stabilizer and/or plasticizer formulation.

Chemical resistance has significance in both formulation and end-use application. Many tests have been developed to simulate field conditions of exposure to alkali, acids, soaps, detergents, sulfides or perspiration. These tests must be used with the same discretion required of accelerated weathering tests. Potential failures or successes may be missed because of inappropriate test conditions (e.g., concentration, timing, film condition) or lack of correlation with end-use performance. Sensitivity to a chemical may become apparent only in combination with exposure to heat, light or moisture. Suitable controls should always be included to differentiate between failure of the pigment and failure of other ingredients.

Chemical stability during formulation, storage and film formation, must also be considered. Reaction between the pigment and other ingredients may produce color or viscosity changes, seeding, rancidity or poor film properties. Replacement of the pigment may not be necessary, however. Systems can be stabilized against troublesome iron and zinc-containing pigments, color change of some azo pigments in plastisols can be overcome by proper resin and stabilizer selection, and seeding in dibasic acid-modified resins might be avoided by dispersing in an acid-free resin first.

PIGMENT PERFORMANCE

A. Yellows

Chrome and iron oxide yellows are the most widely used of this group because of their low cost and acceptable performance in many applications.

Chrome yellows are available over a wide hue range, but the redder shades (medium and light) are generally preferred for their higher strength, greater opacity and superior durability. Chrome yellows are noted for their intense color, ease of dispersion, good acid resistance and non-bleeding qualities.

-16-

Lightfastness is good in thick films where low concentrations can be used, but considerable darkening in masstone and fulling and fading in tint occur at loadings commonly used in solution systems. They discolor similarly in the presence of alkali and soap, and often show more rapid outdoor failure in industrial climates for this reason. Heat stability of the lead chromates is adequate for most vinyl applications; in fact, the lead helps stabilize the resin to heat. However, lead also introduces sensitivity to sulfide staining, promotes rapid settling and restricts use in areas where toxicity is of great concern.

Yellow iron oxides also come in many shades, but all are much duller than the chrome yellows and this limits their application some. The synthetic pigments are more popular than the natural, e.g., siennas and ochers, because of better product uniformity and absence of injurious contaminants. Transparent varieties are now available for use in metallics.

The iron oxides are very lightfast and resistant to chemicals and solvents. However, they tend to lower gloss and gloss retention in solution coatings. Yellow iron oxides are adequately heat stable for most vinyl applications, but they may lose their water of hydration and convert to red iron oxides under severe heat conditions.

Extensive studies indicate the iron in these pigments does not accelerate failure of vinyl under normal circumstances of formulation and use.[4] However, occasional reports of premature discoloration and film embrittlement indicate a need for caution in particularly severe or critical service.

Cadmium yellows represent a large family of bright, non-bleeding colors that are lightfast in full shade, excellent in heat stability, and resistant to soap, alkali and sulfide staining. They are available in both pure and lithopone (barium sulfate extended) forms, with the pure forms being brighter in color.

Cadmium yellows have poor tint lightfastness and are expensive to use at any level because of high price, low strength and moderate opacity. They are also sensitive to acids, which probably accounts for their tendency to spot during exposure.

Benzidine yellows are very transparent pigments which find some application in vinyls because of their bright color, low cost (very high strength) and non-lead composition. However, they have pronounced bleed and crocking tendencies, even in non-volatile systems, and very poor tint lightfastness. Heat stability is also poor in solution coatings.

Nickel azo and vat yellows are relatively high cost pigments used mainly for their superior lightfastness in pastel tints and metallics. The nickel azo, also known as "green-gold", is a very green shade yellow which is resistant to heat, light and chemicals under most conditions, and shows only slight bleed in the stronger solvents. However, high alkalinity or acidity in the formulation can cause demetallization with resulting degradation in lightfastness

and bleed resistance. It is frequently less costly and more light-fast than the vats at equal strength.

The vat yellows, which include acylamino, flavanthrone and anthra-pyrimidine, vary considerably in hue, intensity and transparency. Heat stability is borderline in high temperature applications, and slight bleed may be obtained in solution systems. Color drift in metallics is frequently a problem during storage. Lightfastness in pastels ranges from fair to good depending on the chemical type and formulation.

Quinacridone gold, better known as "Newport gold", is a recent de-velopment which shows its best color qualities in metallics; in tint it is more of a tan than a gold. Lightfastness is good in moderate to dark shades, and resistance to heat, solvents and chem-icals (other than strong oxidizing agents) is excellent. In its present form, this pigment is very difficult to disperse. Chip dispersion is recommended for best results, i.e., transparency, in metallics.

Nickel titanates offer outstanding lightfastness, heat stability and resistance to chemicals and solvents. However, use is limited to applications that can tolerate their very high cost, since strength and hiding are quite low. Also, they are available in light shades only, and produce low gloss in thin films, even at moderate loadings.

Zinc and strontium yellows are used more for their ability to in-hibit corrosion of metals than for their color value. They are weak and low in hiding, and slightly soluble in water. Zinc can also catalyze degradation of some vinyl resins. Basic zinc chromate, also called zinc tetroxy chromate, is a brown used al-most exclusively in a military "wash primer" specification for metal protection; this is in a vinyl butyral system.

Hansa, toluidine and other mono azo dyestuff yellows are rarely used in vinyl systems because of poor heat stability and severe bleed, migration and crocking tendencies.

B. Oranges

Molybdate oranges are particularly popular in vinyl coatings be-cause of their high opacity, low cost, bright color, good light-fastness, excellent heat stability, and non-bleeding properties. Their principal deficiencies are their sensitivity to alkali and soap, which is most evident in tints, and lead content which pre-cludes use in "non-toxic" applications and subjects the coating to sulfide staining.

Shades vary from yellow shade orange to a red. The redder shades are weaker and more transparent, but are widely used in blends with high quality organic reds to replace cadmium reds at con-siderably lower cost and generally equivalent durability. The redder shade oranges are subject to crystal fracture and color change (yellowing) from intensive dispersion, e.g., steel ball milling or chip dispersion; high gloss may also be difficult to

obtain in solution coatings from the redder, larger particle size products.

Cadmium oranges are used primarily for their good lightfastness in near-masstone shades, non-lead content and resistance to sulfide staining. Alkali resistance is also good. They are considerably more costly than the molybdate oranges, however, and tint lightfastness and resistance to mineral acids are poor.

Vat oranges, like vat yellows, are strong but high cost, thus restricting use to pastel tints and metallics. Orange RK is a reddish orange which is particularly attractive for use in metallics because of high transparency when chip dispersed. However, lightfastness, heat stability and bleed resistance tend to be poor in very light shades. Orange GR is a yellower, less transparent orange which offers generally superior performance, but may still be borderline for critical applications. Both are subject to reduction and color drift in metallics.

Quinacridone orange is a very red shade orange with excellent resistance properties, including lightfastness. High cost limits its use to pastel tints and metallics. It is difficult to disperse, but a high degree of transparency can be obtained by chip dispersion, making it particularly attractive in metallics.

Benzidine, pyrazolone and other disazo oranges are used to some extent because of their high strength, low cost and non-lead composition. They are quite transparent in masstone and moderately intense in tint. Chemical resistance is good and heat stability adequate for most applications. However, use is greatly limited by poor tint lightfastness and a tendency to bleed in solvents and plasticizers.

Chrome oranges find little use in vinyls now that they can be matched with blends of molybdate orange and chrome yellow with equal or better properties and lower cost. Since they are basic lead chromates, they are more resistant to alkali but more sensitive to acids than these matching blends.

Hansa, nitraniline and other mono azo oranges, like their yellow counterparts, are too poor in heat stability and bleed resistance to be suitable for use in vinyls.

C. Reds and Violets

Precipitated azos and iron oxides are the most popular of the low cost reds in vinyl coatings. Precipitated azos include permanent red 2B, BON, pigment scarlet, lithol red and rubine, lithol red 2G and Red Lake C. Each of these contains salt forming groups in its molecular structure (e.g., -COOH, -SO_3H) which makes it water soluble until precipitated out with a metal salt. The metal used (e.g., barium, calcium, strontium, manganese) strongly influences color and properties. The high polarity of these pigments makes them resistant to bleed in organic vehicles, but reactive with acids and alkali. Also, the precipitating metal is subject to stripping or replacement by another under some conditions, with an accompanying change in color and other properties. Low cost comes primarily from

the high tinting strength and moderate price of these pigments.

Permanent Red 2B pigments are the most important of the precipitated azos because of their wide range of bright hues, i.e., orange-red to rubine, and general utility in vinyls. Masstone lightfastness is fair, but tint lightfastness is poor, particularly for the barium precipitated orange-red. Heat stability is adequate if allowance is made for temporary bluing that occurs at elevated temperature, and the pigment is used in a chemically stable system.

The blueness that develops with heat is reversible and is believed to be caused by loss of equilibrium moisture, such as from a hydrate, when hot. Immersion of the film in water will hasten recovery of the original color.

A chemically stable system is particularly important with Red 2B pigments because of their reactive salt forming groups and susceptibility to metal exchange as described previously. Drastic color changes that occur during fusing in some plastisol coatings are believed to result from the precipitating metal in the pigment being displaced by a metal from one of the other ingredients, e.g., stabilizer or lubricant. This would account for a bright color of entirely different hue being obtained in some cases rather than the usual darkening, dulling or fading that occurs when the temperature limit of a pigment is exceeded. This reaction appears to require catalysis since it has been observed only with plastisol resins in which residual polymerizing or emulsifying agents are known to be present.

Red 2B pigments are well known for their tendency to plate-out on metal surfaces of processing equipment, e.g., calenders or embossing rolls. This is frequently accompanied by bronzing and crocking. The small particle size and highly polar nature of these pigments appear to give them a strong affinity for metal surfaces at high temperatures. Plate-out tendencies can be reduced by introducing an organic layer between the dry pigment and metal such as by predispersing the pigment in plasticizer, wiping the metal surface with plasticizer or lubricant, or increasing the lubricant concentration. A change in stabilizer or plasticizer may also help.

Some forms of Red 2B pigment contain appreciable quantities of rosinated extenders. These are likely to cause seeding or gelation of systems containing vinyl resins with free carboxyl groups.

BON reds are manganese precipitated Red 2B pigments which are often classified separately because of some important differences in properties. Their hues range from intermediate shade red to maroon, but they are noticeably duller than comparable shade Red 2B pigments. The BON reds offer better lightfastness at all levels, although they can be rated good only in near-masstone shades. Inherent heat stability is somewhat poorer than the Red 2B pigments, and they show the same bluing and reactivity tendencies at high temperature. Plate-out, bronzing and crocking properties are also similar.

Because of their manganese content, BON reds can promote rancidity

in systems containing plasticizers or stabilizers with appreciable unsaturation or tertiary carbon atoms. Castor oil derivatives are particularly susceptible; tall oil and soyabean oil plasticizers may also be affected.

Pigment scarlet and lithol rubine are bright, blue shade reds having many of the same characteristics of Red 2B pigments, e.g., high strength, good bleed resistance, tendency to plate-out, reactivity with other ingredients at high temperature (otherwise good heat resistance) and temporary bluing while hot. They are stronger and lower in cost than Red 2B pigments but poorer in lightfastness.

Pigment scarlets frequently contain zinc oxide which can accelerate degradation of zinc-sensitive vinyl resins. Pigment scarlet is also a notoriously hard textured product, thus requiring special attention to dispersion.

Lithol rubine is frequently rosinated to give better dispersion and color properties. Such treatment can cause seeding and gelation of solution systems made with resins containing free carboxyl groups.

Lithol reds rarely find use in vinyl coatings because of very poor light, heat and chemical stability. Lithol Red 2G, an isomer of Red 2B, is only moderately superior to lithol red in these respects and offers no outstanding features that would make it competitive with other low cost reds.

Red Lake C has adequate heat stability, but very poor lightfastness and chemical resistance. It may also bleed in some systems.

Iron oxide reds, like the yellows, are available in many shades and in both transparent and opaque forms. However, all are much duller than most organic reds, thus limiting use somewhat. The iron oxides are very resistant to heat, light, chemicals and solvents, and lowest in cost of any of the reds. Gloss and gloss retention are impaired as loading increases, particularly in solution systems. Like the yellows, the iron in these pigments appears to have no deleterious effect on the life of the film because of its strong chemical bond in the pigment; however, careful testing is advisable in particularly critical or sensitive applications.

Cadmium reds and maroons are popular primarily because of their good lightfastness in a variety of bright masstone shades. They also offer excellent heat stability, are non-bleeding, and are resistant to alkali, soap and sulfide staining. However, they are expensive to use at any concentration because of high price and low strength, and their color becomes quite dull when tinted. Cadmiums are sensitive to mineral acids and frequently spot on exposure in industrial atmospheres.

Quinacridone red, violet and maroon pigments combine bright color and high transparency (for metallic use) with excellent resistance to heat, light, solvents and chemicals (other than strong oxidizing agents). High cost tends to limit use to low concentrations. Nevertheless, the violet is widely used in blends with molybdate orange to replace cadmium reds at considerably lower cost and generally equivalent durability; however, the molybdate orange

introduces increased sensitivity to alkali and sulfide staining and presence of toxic lead. Because of their high strength and light-fastness, the quinacridones can be used in very low concentrations to tone other lightfast pigments (titanium dioxide, iron oxides, phthalocyanines) without sacrifice in durability or significant increase in cost. Some quinacridones tend to be hard dispersing and chip dispersion may be necessary to get desirable metallic effects.

Perylene, thioindigo and related products occasionally provide a satisfactory balance of properties at lower cost than the quinacridones. This is generally true in medium to dark shades where light-fastness and heat stability approach those of the quinacridones, and cost becomes critical.

The perylenes are very high strength reds and maroons that find principal use in metallics because of excellent transparency; they have moderate to low color intensity in tint. Lightfastness and heat stability are poor in pastels but improve considerably with increasing concentration. Chemical and bleed resistance are good.

Thioindigo reds and violets are brighter in tint color than the perylenes, but are generally inferior in lightfastness and heat stability. In addition, some shades bleed badly.

Pyrazolone reds are very high strength, low cost, bright and transparent colors. However, very poor lightfastness (except in masstone) and poor heat stability greatly limit their application in vinyl coatings. They may also bleed in some systems.

Toluidine, para and arylide reds are rarely used in vinyl systems because of severe bleed and poor heat stability. Lightfastness is also poor except in full shade.

D. Blues

Phthalocyanine blues are decidedly the most popular of the blues because of their high strength, low cost, bright color and generally excellent fastness to heat, light, chemicals and solvents. They cover the intermediate to green shade range, and are suitable for use in either tint or metallic. The green shades differ in crystal form and are generally more stable than the red shades. Phthalocyanine blues have a very dark masstone color and tend to bronze on exposure in dark shades. Lower cost, crystal unstable red shades are available which may perform satisfactorily in non-volatile systems, but are likely to lose strength in solvent systems, especially at elevated temperatures.

Flocculation and/or flooding may occur in fluid systems, particularly in the presence of strong polar solvents, which can adversely affect strength, opacity, color and even durability. Various treatments are used to confer flocculation resistance on the pigment, but performance is still highly dependent on the system in which it is used. Rosination is frequently used to improve dispersion; such treatments are likely to cause seeding or gelation of systems in which a vinyl resin containing free carboxyl groups is used. Phthalocyanine blues reportedly do not have adequate heat and light stability at extremely low concentrations for some applications, thus requiring the use of more expensive blues.

Indanthrone blues are considerably redder and duller in shade than the phthalocyanines. High cost limits their use to pastel tints and metallics where they show good lightfastness but only fair heat stability. They also have a tendency to bleed in some systems and are susceptible to chemical reduction in metallics.

Ultramarine blues are noted for their bright, red shade tints. They are very heat stable and bleed resistant, and show good lightfastness in non-acid atmospheres. However, extreme sensitivity to mineral acids and high cost severely limits their use.

Cobalt aluminate and other metal oxide blues offer excellent fastness properties but are quite expensive because of very low tinting strength. A variety of shades are available, but these usually can be matched with low cost, high quality phthalocyanines. The metal oxide blues are frequently difficult to disperse.

Iron blues fall in the same tint color range as the phthalocyamines, but suffer by comparison in most respects, including cost. Iron blues are extremely sensitive to alkali. Furthermore, the iron in these pigments catalyzes degradation of vinyl resins.

E. Greens

Phthalocyanine greens rank as the most stable of all organic pigments by virtue of their excellent fastness to all processing and environmental conditions that might reasonably be encountered. A wide shade range is available. Principal use is in tints and metallics where their bright color and high strength gives them a pronounced advantage over inorganics of similar fastness characteristics. Lower cost greens of similar color can be obtained from blends of phthalocyanine blue and a yellow, but property deficiencies of the yellow must be reckoned with.

Pigment Green B is very dark in masstone and olive-green in tint. It finds limited use in vinyl because of its single, dull shade and relatively poor tint lightfastness. The iron in the pigment might promote vinyl degradation under severe conditions, although no marked tendency has been detected in normal application. This product offers excellent alkali resistance and is non-bleeding.

Chromium and other metal oxides are similar to the phthalocyanines in offering excellent fastness properties, but are generally duller and much weaker and more expensive to use. Many are difficult to disperse.

Chrome greens are intimate physical mixtures of chrome yellow and iron blue, and, therefore, have many of the inherent characteristics of these constituent pigments as already described. Hiding is very high and cost is low. Use is limited primarily because of the degradative effect of the iron on vinyl resins.

CONCLUSIONS

Pigments should be selected for their effect on cost and performance as well

as color. No pigment is completely trouble-free in all applications, although the phthalocyanines and quinacridones offer greater formulating latitude than others because of generally outstanding color and performance. Other pigments, less versatile because of certain deficiencies, can still be used in many applications where their weaknesses are of little importance or are offset by particularly desirable characteristics.

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THERMOSETTING VINYL-URETHANE REACTION PRODUCT

FOR USE ON EXTERIOR WOOD PRODUCTS

Norris Legue

Technical Service Department

The Baker Castor Oil Co.

Bayonne, N. J.

INTRODUCTION

The present demand for prefinished wood siding is due primarily to two over-riding factors that have been forcefully brought to the attention of the wood man-ufacturers by the intense competition offered by non-wood products such as alumi-num siding, asbestos shingles and plastics siding.

1. The overall economics of prefinished siding is more faborable than for siding finished on-site. Thus, lower initial labor costs plus a longer serviceable life (longer time spread be-fore recoating becomes necessary) gives prefinished siding distinct pricing advantages. Prefinished lumber also permits faster as well as all-weather construction.

2. Factory finishing of siding also offers many inherent technical advantages. Questionable on-site workmanship, variable and un-controllable weather conditions, uncertain applied film thick-ness, and the use of weathered lumber during on-site construction can all contribute to premature film failure. Factory finishing, in addition to eliminating the above problems, permits the use of superior industrial finishing systems. Industrial coatings are not normally applicable to on-site applications because of such demanding requirements as strong solvents, accurate mixing (if two package), controlled application conditions, baking demands, and application (usually) by non-brushing methods.

One of the most promising type finishes developed for the factory priming of wood is a thermosetting coating comprising a hydroxy-containing vinyl resin, a castor oil derived polyol and a castor oil derived urethane prepolymer

DISCUSSION OF THE PROBLEM

Aluminum siding manufacturers guarantee finished aluminum for periods in excess of ten years. Therefore, finishes are commercially available that are capable, in themselves, of withstanding prolonged weathering conditions. The substrate, however, is often a more decisive factor in film performance than the weather in determining ultimate service.

With metals, such factors as the type of metal, the metal surface preparation (phosphate treatment, chromate treatment, sand blasting, degreasing) incipient rusting and coating adhesion to the substrate, affect performance.

Wood presents an even more complex substrate with associated problems. For example, no two pieces of wood are exactly the same. Temperature, humidity, sun and other climatic conditions affect both the physical and the chemical properties of wood during its growth period. The section of the tree that grows during the summer is far different than the section that grows in the spring. The grain (alternating bands of dark and light wood) is also highly variable. These factors contribute to the dimensional instability and variability of the wood, particularly when the wood is water soaked and dried, which in turn tends to adversely affect the performance of the finish.

As an example, consider a coating applied to the face of two different 3" x 6" pieces of 3/8" thick exterior plywood undercontrolled conditions (method of application, film thickness and cure are the same). Both panels were subjected to 25 cycles of the American Plywood Association's boiling water test and examined. The coating on one panel had film ruptured amounting to over 25" of accumulative measurement, whereas the other had no film ruptures. The difference was due entirely to the substrate. One coating was applied to a dimensionally stable piece of wood which was characterized by a very tight grain (a very thin band of dark wood, followed by a very thin band of light wood, followed by another very thin band of dark wood). Conversely, the coating with over 25" of film ruptures was applied to wood with poorer dimensional stability (very wide grain). In addition to having bands spread far apart, the wood with the poor dimensional stability (Figure 1) was primarily composed of dark bands that are normally hard and less stable. They are also difficult to adhere to because of this greater hardness (preventing penetration).

The American Plywood Association has designed accelerated laboratory tests that closely reproduce the dimensional changes that can be anticipated after many years of exposure. Plywood panels coated on one side only and with no edge or back sealing are subjected to three cyclical water soak tests as follows:

1. Soak Test: Two 3" x 6" panels are subjected to 25 cycles of
    eight hours immersion in ambient temperature water followed by
    drying 16 hours in an oven at 145°F.

2. Boil Test: Two 3" x 6" panels are subjected to 25 cycles of four
    hours immersion in boiling water followed by drying 20 hours in
    an oven at 145°F.

3. Freeze Test: Two 4" x 6" panels are subjected to ten cycles of
    eight hours immersion in ambient temperature water, followed by
    16 hours freezing at 0°F or lower, followed by 24 hours drying
    in an oven at 145°F.

After being subjected to the test, the coating should have no extensive loss of adhesion, no blisters and any coating ruptures must be no more than 6" of cumulative measurement. There should be no extensive chalking, discoloration or overall appearance degradation.

Of the three water immersion tests, the boiling water test is by far the most severe. An uncoated piece of wood that has been subjected to this test is usually severely warped and cracked. The length of the cracks sometimes runs

from 4" to 6", the crack widths sometimes amounting to greater than 1/8" or 1/4" and in some cases, the wood on one side of the crack is often raised higher than the wood on the other side of the crack. In summary, the wood substrate, after the water test, is quite different than before the test. Its dimensions are different, its surface is non-uniform. The other two tests are generally not considered as severe as the boiling water test. However, they too cause dimensional changes and if a paint passes them it also insures that the coating will perform well over a wide temperature range.

MAJOR REQUIREMENTS OF PAINTS FOR FACTORY FINISHED SIDING

There are at least three major requirements that a coating must meet to be considered acceptable for factory finishing and subsequent marketing.

A. It Must Withstand The Wood's Dimensional Changes

It should be understood that a coating applied to wood does not prevent the dimensional changes (previously described) from taking place, rather it adjusts to them. For a coating to perform well on such an unstable substrate, it must have outstanding adhesion, co-hesion, and excellent flexibility so that it can expand and con-tract with the wood substrate. It must be able to bridge the cracks without tearing and it must have outstanding water resist-ance to withstand immersion in boiling water, ambient temperature water and ice, for long periods. Figure 2 shows what occurs when a vinyl urethane coated piece of plywood is subjected to the boil test. Note that it bridges all cracks that developed in the wood.

B. It Must Have Excellent Exterior Durability

Whether serving as a self-priming top coat or as a primer, a coating must have both excellent initial and aging properties to withstand weathering for ten or more years. For self-priming top-coats, excellent adhesion, cohesion, flexibility, tear strength, water resistance, lack of gradual embrittlement and resistance to the effects of sunlight are essential. With primers, resistance to sunlight is less necessary. However, inter-coat adhesion be-tween primer and top coat is mandatory.

C. It Must Lend Itself to Production Line Finishing

In order to maintain mill capacity and retain its economic ad-vantage, a finish must be suitable for production line finishing. Application and curing within a few minutes are essential.

VINYL-URETHANE SOLVES THE PROBLEM

Not many coatings meet the requirements previously described. Of all those evaluated, only a pigmented vinyl-urethane coating (EC-167) has successfully passed all three water immersion tests (DFPA trademark Grade A-C and Medium Den-sity Over-Laid Plywood). It also appears to handily meet the B. and C. require-ments above of durability and suitability for production line finishing.

This pigmented vinyl-urethane coating is a two-package system containing a vinyl chloride-vinyl acetate-vinyl alcohol copolymer and a castor oil derived

polyol in Package A. The castor oil derived urethane prepolymer is Package B. Typical properties for the three products are listed in the Appendix. The formulation and physical constants for this pigmented vinyl-urethane coating prepared from these three base products are given in Table I. Performance of this formulation in various tests is shown in Table II.

UNIQUE CHARACTERISTICS OF THE PIGMENTED THERMOSETTING
VINYL URETHANE FORMULATION (EC-167)

In addition to being the only coating that meets the above listed test requirements for either DFPA trademark Grade B-C (or better) Exterior Plywood or DFPA trademark Medium Density Overlaid Plywood, this pigmented vinyl-urethane formulation had added distinguishing features.

It is a total finish (self-priming top coat). Most conventional coatings with good weathering properties require a primer for adhesion. Conversely, conventional primers require the protection of top coats to prevent rapid weather degradation. In addition to the obvious advantages associated with using one system instead of two, longer weathering can be expected from a self-priming top coat. The entire film has good weathering properties, whereas at the same film thickness for a primer plus a different top coat system, only the top coat has good weathering characteristics. It should further be noted that exposure tests show that this vinyl-urethane coating can also serve as an excellent primer per se for solution vinyl, alkyd, acrylic latex, vinyl acetate latex and oil base top coats.

FACTORS AFFECTING PERFORMANCE

A. Film Thickness

The performance of the pigmented vinyl-urethane system depends heavily on film thickness. Generally, 5 mils is satisfactory on sanded plywood. On extremely poor wood, that is to say, one with very wide bands and containing the major percentage of dark wood, a film thickness above 5 mils is necessary in order to pass the 25 cycles of the American Plywood Association boiling water test.

Since the water soak and freeze tests more closely approximate the temperature variations that can be expected during weathering, film thickness studies were initiated to determine how long it would take for the pigmented vinyl-urethane to fail in these tests. As of this writing, 97 cycles in the soak tests and 48 cycles in the freeze test have been completed. Results are excellent as shown in Table III.

Weathering tests also indicate that 5 mil thickness on sanded plywood and $3\frac{1}{2}$ mils on overlaid plywood is quite satisfactory. In summary, the thicker the film, the better the performance of the vinyl urethane coating on wood. For most woods, a 5 mil film is satisfactory. For extremely poor wood, a film thickness of 5 mils or greater is necessary in order to pass 25 cycles of the American Plywood Association boiling water test without any film rupture. Under conditions that can be expected during normal weathering, 5 mils appear satisfactory on all wood grains.

For more dimensionally stable substrates such as overlaid plywood and hardboard film, thicknesses of about 2 mils are satisfactory for the water soak tests. However, for long term weathering, $3\frac{1}{2}$ mils or greater is recommended.

B. Cure

The pigmented vinyl-urethane coating (EC-167) may be air dried, forced dried or baked. It becomes tack-free as soon as the highly volatile solvents evaporate. Actual curing to a three-dimensional type structure is dependent on time and temperature. No direct cure time versus temperature relationship has been established. However, the figures listed in Table IV will give an indication of approximate cure rate.

Actually, complete curing during baking is not necessarily a mandatory requirement since most prefinished products are seldom used immediately after coating. Continuation and completion of cure will occur later at ambient temperatures during storage and shipping. It should also be noted that an upper temperature limitation on cure may be more dependent on the ability of the substrate to withstand heat than the vinyl-urethane itself. EC-167 shows no niticeable yellowing after baking at 400°F for 10 minutes.

C. Sanding

There is no noticeable difference in performance between a panel that has been sanded and one with no sanding. However, appearance is improved if the panel is touch-sanded. The best procedure is to touch-sand after the first coat of the pigmented vinyl-urethane has been applied. The first coat locks the wood or paper fibers in place and touch-sanding at this stage removes any fibers that protrude above the surface of the paint.

APPLICATION

For appearance purposes, it is best to apply the pigmented vinyl-urethane coating (EC-167) in two or more coats. Applying the first coat at $1\frac{1}{2}$ to 3 dry mils appears to give the best results. The second coat may be as high as 5-6 mils. EC-167 may be appplied using a conventional spray gun, airless spray gun or curtain coater. Approximately 2 to 3 dry mils per coat can be applied using a conventional gun and 4-6 dry mils per coat using an airless spray gun or curtain coater.

FUNCTION OF MATERIALS

The vinyl resin is a high polymer vinyl-chloride, vinyl acetate, vinyl-alcohol copolymer with good durability and fast dry. It provides hydroxyl groups that react with urethane prepolymers.

The polyol is a castor oil derived product that complements the functions of the vinyl resin. It also provides hydroxyl groups that react with the urethane prepolymer. It enhances flexibility, toughness and durability.

Titanium dioxide is a very small particle size white pigment with excellent

hiding power and good brightness. It is highly resistant to chalking and fading on exterior exposure.

Antimony oxide is a white pigment that helps to prevent chalking, improves suspension properties (when used in conjunction with titanium dioxide), and contributes fire resistant properties.

The lecithin grinding aid is a highly purified type of lecithin with a carrier of fatty oil designed for improved dispersing action.

Diglycidyl ether of Bisphenol A is an epoxy resin commonly used for stabilizing resins containing vinyl chloride.

The alkyd/silicone combination by modifying the film surface properties allows gases and vapors to escape without causing bubbles or blisters.

The urethane component is a castor oil derived prepolymer with terminal isocyanate (NCO) groups. A three dimensional type structure is formed when it reacts with the hydroxyl groups of the vinyl resin and the castor derived polyol. The castor urethane prepolymer is designed to give the optimum balance of thermoplastic and thermoset properties that is necessary to impart excellent exterior durability and outstanding performance in the water soak tests.

MODIFICATIONS

A pigmented vinyl-urethane coating as exemplified by the given formulation (EC-167), is an excellent finish for overall performance. However, it is recognized that modifications to improve a specific property may become necessary for certain applications and/or for specific types of application equipment. Some modifications and the changes that can be expected are listed.

A. Selection of Solvents

A wide variety of ketone and secondary solvents can be used to change drying properties, viscosity, pot life and the like. For example, replacing all or part of the MIBK and/or toluene with methyl ethyl ketone (MEK) will reduce tack free time, increase pot life, and lower solution viscosity as shown in Table V for EC-167.

B. Change in Pigment Volume Concentration (PVC)

The PVC can be changed while keeping the ratio of titanium dioxide to antimony oxide constant. As the PVC is increased, dry time, block resistance, hiding power and hardness improve. Flexibility, chalk resistance and performance in the water soak tests degrade. However, the adverse effects are not very great when the PVC is kept below 40%. This is particularly true on dimensionally stable substrates such as overlaid plywood and hardboard.

Decreasing the PVC gives better flexibility and performance in the water soak tests. However, if the PVC is decreased to any great extent (say below 17%), a top coat is needed to protect the vinyl-urethane vehicle from ultra-violet light degradation.

C. Vehicle Modifications

The per cent vinyl and per cent pigment can be kept constant while varying the amount of castor oil derived polyol and castor oil derived urethane used. This is easy to do because both have the same non-volatile concentration. For example, 100 parts of EC-167 paint contains 7.20 parts of polyol and 5.53 parts of urethane prepolymer. If 6.2 parts of the polyol (decreased by 1 part) and 6.53 parts of the urethane prepolymer (increased by 1 part) were used, more thermosetting properties can be expected. The coating will dry faster and harder while flexibility and pot life will degrade. The per cent vinyl can also be varied. The vinyl can be increased while keeping the ratio of polyol and urethane prepolymer constant or while lowering the per cent of polyol used. In the latter case, approximately 1.3 parts of polyol will be removed for every part of vinyl added. Both modifications will give faster dry and more high polymer type properties. Conversely, decreasing the per cent vinyl and increasing the urethane prepolymer and/or polyol will give slower dry and more urethane-type properties.

SUMMARY

Polymer manufacturers, the paint industry and the lumber industry are all expending a great deal of effort into the testing and development of wood finishes that will be suitable for production line finishing and that will have ten years guaranteed durability. However, the dimensional instability and variability of the wood substrate makes this a difficult goal to achieve as demonstrated by the inability of previous coatings to pass the three preliminary water soak tests designed by the American Plywood Association. These tests quickly and effectively demonstrate whether a finish can withstand the dimensional changes that can be anticipated after years of exterior plywood exposure.

A pigmented vinyl-urethane coating system has been developed specifically to meet the extremely rigid water soak requirements of the American Plywood Association on various grades of exterior plywood and overlaid plywood. In addition to meeting the water soak requirements, this coating has excellent exterior durability and appears to lend itself to production line finishing. It should serve as an excellent total finish (self-priming top coat system) for sanded plywood, overlaid plywood, composition board and hardboard. It is also an excellent primer for conventional top coats.

ACKNOWLEDGMENTS

APPENDIX

TYPICAL PHYSICAL AND CHEMICAL PROPERTIES

OF BINDER RAW MATERIALS (25C)

	Vinyl Resin (Vinylite VAGH)*	Castor Polyol (Polycin 172)	Urethane Prepolymer (Vorite 174)
Color, Gardner (1933)	White powder	2+	3
Acid Number	-	.3	-
Density (9/cm^3)	1.39	1.00	1.01
Ref. Index	-	1.446	1.501
Viscosity (Stokes)	-	.90	1.58
Viscosity (Gardner bubble)	-	C+	G-
Viscosity (Intrinsic)	0.57 (20C, cyclohexanone)	-	-
Non-Volatile, %	100	75	75
Volatile		2-ethoxy ethyl acetate	MIBK/Toluene 1:1
-NCO, %	0.0	0.0	7.5

*Vinyl chloride 91%, vinyl acetate 3%, vinyl alcohol 6%

TABLE I

Formulation Number EC-167

Part A

	Weight
Vinyl chloride-vinyl acetate-vinyl alcohol copolymer (VAGH - Union Carbide Plastics Company)	11.70
Castor oil derived polyol (Polycin[R] 172 - Baker Castor Oil Co.)	7.20
Titanium Dioxide (Non-chalking - Rutile)	19.45
Antimony Oxide (White Star Grade - National Lead Co.)	2.15
Grinding Aid (Lexinol AC-1 - American Lecithin Co.)	0.21
Diglycidyl Ether of Bisphenol A (ERL-2774 - Union Carbide Plastics Co.)	0.66
Alkyd (Duraplex D-65A - Rohm & Haas)	0.09
Silicone (Dri-Film 103 - General Electric Co.)	0.01
Methyl Isobutyl Ketone	26.50
Toluene	26.50
Sub-Total	94.47

Procedure for Part A

1) Dissolve VAGH, Duraplex D-65A, Dri-Film 103 and ERL 2774 to MIBK: toluene.
2) Charge pigments, Lexinol AC and 12 parts of above solution to a pebble mill and grind to a fineness greater than 5. (It is essential that the pigment be ground in the vinyl solution rather than in the polyol. The vinyl solution should never be left out of the original grind.)
3) Reduce grind with remaining solution (1) and add Polycin 172.

Part B

Castor oil derived Urethane prepolymer (Vorite[R] 174 - Baker Castor Oil Co.)	Sub-Total	5.53
	TOTAL	100.00

Procedure for Preparing Paint for Application to Wood

1) Mix Part A and Part B thoroughly.
2) Reduce to spraying viscosity with MIBK: toluene 1:1 as necessary

Properties	Weight Basis	Volume Basis
Non Volatile	43.8	26.3
Volatile	56.2	73.7

Pounds per Gallon	9.2
Pigment Volume Concentration	21.3
Per cent Pigment by Weight	50
Viscosity (Krebs Units)	62

TABLE II

a) AMERICAN PLYWOOD ASSOCIATION WATER IMMERSION TESTS

Panels spray coated and baked at 180°F for 20 minutes.

	Results for EC-167 on DFPA Sanded Plywood (Grade B-C) or better and DFPA Medium Density Overlaid Plywood
Boil Test - 25 cycles of 4 hours total immersion in boiling water followed by 20 hours dry an oven at 145°F	No loss of adhesion No blisters No film ruptures

Figures 3 and 4 show the performance of a typical commercial paint versus EC-167 when subjected to the boil test.

Soak Test - 25 cycles of 8 hours total immersion in ambient temperature water followed by 16 hours in an oven at 145°F	No loss of adhesion No blisters
Soak Freeze Test - 10 cycles of 8 hours total immersion in ambient temperature water, followed by 16 hours at 0°F, followed by 24 hours in an oven at 145°F.	No loss of adhesion No blisters No film ruptures
b) EXTERIOR WEATHERING (1 year at 45° south)	No major change
c) WEATHEROMETER (equivalent to 10 years exposure)	No major change

- -

TABLE III

Substrate	Mils of EC-167	25 CYCLES APA Boiling Water Test	97 CYCLES APA Water Soak Test	48 CYCLES APA Freeze Test
DFPA trademark	2	OK	OK	OK
Medium Density	3	OK	OK	OK
Overlaid Plywood	5	OK	OK	OK
DFPA trademark Exterior Grade	3	12" or more of film rupture	Only 8" of film rupture	Only 2¼" of film rupture
A-C Plywood	5	OK	OK	OK
	7	OK	OK	OK

- -

TABLE IV

Temperature, °F	Approximate Cure Time
50	48 hrs.
77	16 hrs.
180	20 min. (.33 hr)
225	10 min. (.166 hr)
300	4 min. (.067 hr)
350	2 min. (.033 hr)

TABLE V

Test	Solvent MIBK:Toluene 1:1	Solvent MEK
Tack Free Time, minutes @ 77°F	7	2
Viscosity, Initial (KU)	62-	53
1 hour	62	53
2 hours	67	53+
3 hours	72	53+
10 hours	82	54
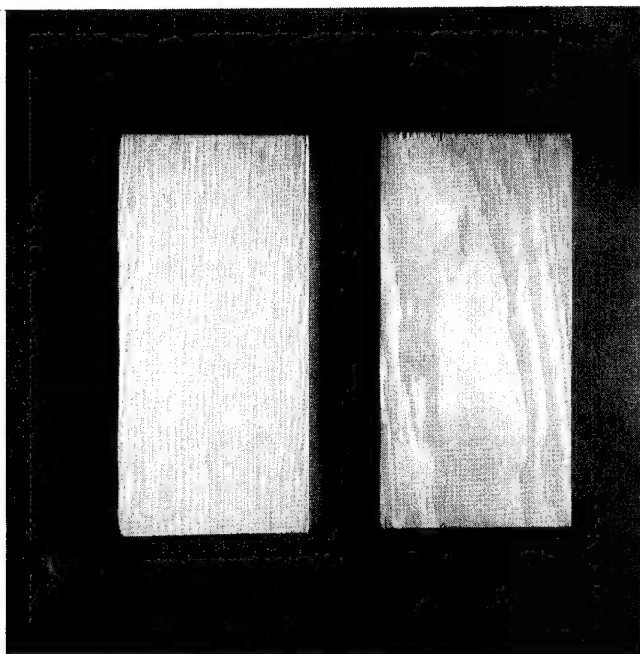
FIGURE 1: Edge Grain Panel with Good Dimensional
Stability (left). Flat Grain Panel with
Poor Dimensional Stability (right).
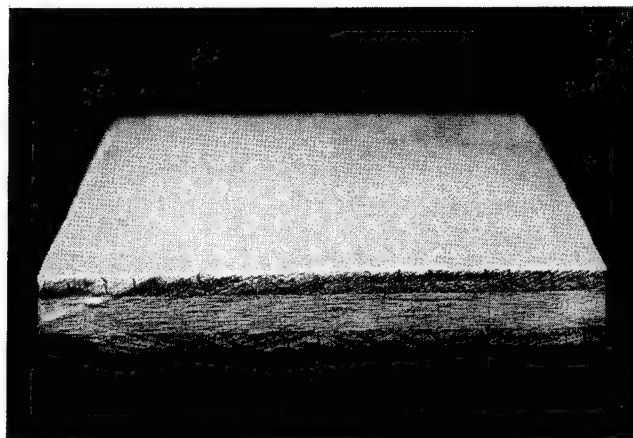
FIGURE 2: Side View of EC-167 Coated Plywood Panel
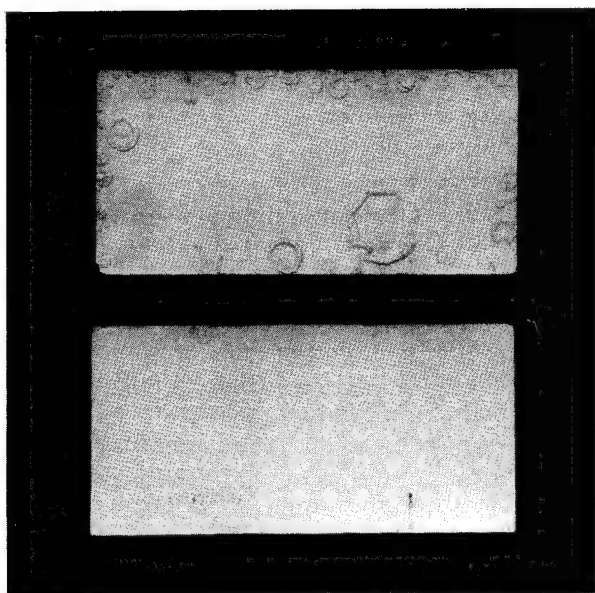
FIGURE 3: 25 Cycle Boil Test — Conventional Com-
mercial Finish (top) Versus EC-167 Coated
Over Laid Plywood (bottom).
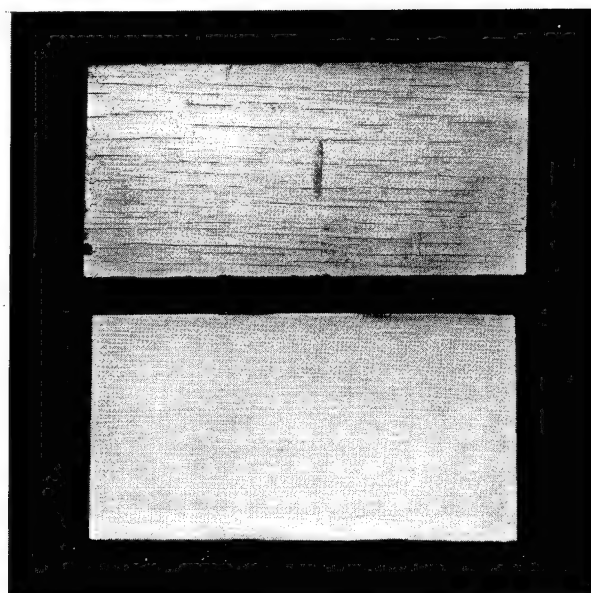
FIGURE 4: 25 Cycle Boil Test — Conventional Com-
mercial Finish (top) Versus EC-167 Coated
Bare Plywood (bottom).

VINYL MARINE COATINGS IN THE U. S. NAVY

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INTRODUCTION

Vinyl resins are well established in the coatings industry and have certainly made a spectacular contribution in the surface protection field. It is estimated that in 1963 about 45 million pounds[1] of vinyl resins were used in the various types of coatings. Along with American industry and the American public the U. S. Navy has been a good customer for vinyls.

The vinyl resins include the water-dispersed or latex type which is used extensively for interiors and exterior surfaces; solvent solution type which makes up some of the best maintenance and finish coatings for metals; and the vinyl organosol or plastisol type that provides tough resistant coatings for metal items. One new use for vinyl is as a material for damping vibrations or sound. Another novel use is the application of a clear coat of vinyl over bare metal surfaces to maintain appearance. For example, the present shiny scratch-free look of the high school band sousaphone is probably because of the protection offered by a coat of clear vinyl.

All types of vinyl resins have been used by the U. S. Navy and some are widely used at the present time. Experiments were conducted with certain polyvinyl acetate latex type vinyl coatings to "deaden" sound in areas of the superstructure of submarines where "drumming" is a problem. Also blocks or tiles of the vinyl resin have been formed and installed to reduce noises from motors, pumps and other equipment. Also vinyl tile is used for interior decking surfaces. Certain vinyl latexes are used for painting the interiors of submarines where solvents would contaminate the atmosphere and interfere with the carbon dioxide scrubbers. Solvent type vinyl coatings have been used extensively for 15 years on the exterior topside and underwater areas of submarines. Vinyl shipbottom paints are also being used on surface ships. Saran (copolymer of vinylidenechloride and acrylonitrile) was used extensively for years for coating fuel and salt water ballast tanks. The plastisol type vinyl has been used to coat levers and wheels for valves and other equipment, for brackets and braces and tool grip areas.

Certain deficiencies which seem to be inherent with high linear polymer type film formers manifest themselves with the vinyls, too. Porosity or entrapped air bubbles is one defect which is common with Saran and other vinyl materials. Most vinyl solvent formulations have relatively low flash points which produce a hazard and an added cost for safety precautions to prevent any such hazard from occurring. Adhesion was a problem with vinyl coatings, but with #117 wash primer excellent adhesion has resulted. Because of the high molecular weights of most of the

vinyl resins used in solvent coatings, only thin films can be built-up per coat, thus the ordinary coating system for sea water emersion requires multiple coats to acquire the 6 or 10 mils that are needed for protection. Also good surface preparation is necessary which is a decided added cost. Although some compromises have been announced in surface preparation, still the best performances are obtained from good surface preparation.

In spite of these deficiencies vinyls have continued to be used in the Navy. In recent years studies have been made in the Navy laboratories to understand the causes of certain of these deficiencies and how to overcome them. Considerable progress has been made in eliminating porosity and thus being able to apply non-porous dense film. With dense films the requirement for excessive thick films is eliminated. Also, with a conspicuously blue-colored wash primer there is less chance for holidays or invisible thin films. Wash primer must totally cover the surface in order to promote adhesion of vinyl coatings on metals. Also, high flash solvents have been incorporated in standard vinyl formulations and thus the explosive hazards lessened considerably. Certain of these formulations can be carried on board ship since they have high flash points.

In reviewing vinyls in the Navy, particular emphasis will be placed on the polyvinyl chloride, polyvinyl chloride-acetate and vinyl alcohol modified polyvinyl chloride-acetate types of vinyl resins. The polyvinyl butyral is heavily involved since this resin is the wash primer base. Saran can be considered as a vinyl material. Although its present use in tanks is limited because of chemical coatings such as epoxies, a revival of a Saran via a high flash formulation is evident. The introduction of zinc dust in the first coat of high flash or safety solvent Saran has improved corrosion protection remarkably, completely eliminating the usual pinpoint rust spots.

As a general statement, we may view the whole problem of painting in the Navy with a question - Why do we paint?

Briefly, in the ocean the ship is confronted with two enemies or two destructive environmental problems - one of corrosion and the other of fouling. To combat both of these, we have to understand something about them, especially how they persist.

THE CORROSION ACTION

In all the deterioration processes the rusting of iron is probably the most classical and goes about in two ways - dry corrosion where there is a direct combination between metal and non-metal elements (oxygen, sulfur, halogens), and wet corrosion where the metal dissolves and replaces hydrogen in water and acid or replaces another metal in a salt solution.

The wet process, the type that goes on in the ocean and marine environment, is by far the most prominent in nature. A summary reaction for the formation of rust can simply be written as:[2]

$$4Fe + 3O_2 \xrightarrow{H_2O} 2Fe_2O_3 \cdot X\ H_2O$$
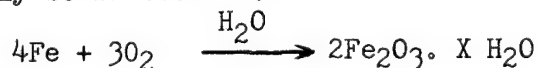
The general nature and mechanism of corrosion of iron may be stated:

1. Iron will not corrode at normal temperature in the absence of moisture.

2. Oxygen helps to accelerate corrosion. In natural water, the rate of

corrosion is almost directly proportional to the oxygen concentration.

3. The products of iron corrosion are black ferrous oxide and green ferrous hydroxide next to the metal and a reddish brown ferric hydroxide which forms the outer layer with graded mixtures of the products in between. When iron corrodes in the atmosphere the amount of ferrous products is small due to the abundance of oxygen and in water the amount of ferrous products is large due to the limited supply of oxygen. This is readily recognized when loose paint is removed from the bottom of a ship when it first docks. The black ferrous oxide or green ferrous hydroxide soon picks up extra oxygen and turns to the reddish brown ferric oxide.

In the common rusting of iron, it is essential that moisture be present. If oxygen is also present, the corrosion is accelerated. It is recognized by the electrochemical theory of corrosion of iron[3] that the surface displays anodic and cathodic areas[4] which make possible the rapid deterioration of the anodic areas in sacrifice for the protection of the cathodic areas.

To cope with the corrosion of iron then, it is only necessary to keep moisture and oxygen away from the iron. One common method is to seal off the iron with an impermeable membrane or coating.

In shipbuilding, the fight against corrosion begins at the plate racks. Here in a matter of a few months the millscale mechanically cracks and permits moisture to reach the base iron. Since the millscale is cathodic and the iron anodic, a galvanic cell is set up with iron being sacrificed. If the action is permitted to continue, the plate develops deep pits and eventual perforations.

Figure 1 shows the corrosion action taking place on the surface of the steel plate. Figure 2 shows what has been done to cope with the corrosion action. The plate has been abrasive blasted or acid pickled and a coat of a shop primer such as Formula 84, zinc chromate applied.

THE FOULING PROBLEM

Beside the corrosion action, the ocean and marine environment present the fouling problem. Like corrosion, fouling is a costly attack on man's endeavors in and on the ocean. Fouling can contribute to the mounting dollars lost to corrosion by promoting corrosion. Hydrogen sulfide produced by decay processes from dead marine growth can attack iron. Oxygen-concentration cells can be formed under certain encrusting marine attachments and cause galvanic corrosion of iron.

Aside from the corrosion aspect, fouling itself can decrease the speed of a ship and cause an over-consumption of fuel. Conduits or pipes carrying sea water can be filled up with marine growth such that the water flow can be completely choked off. Certain sound detecting devices can be forced inoperative because of fouling. Buoys and navigational units can accumulate excessive amounts of marine attachments causing them to shift or break away.

One practical and economical way to cope with foulding is by applying anti-fouling coatings. This the Navy has done successfully with their effective ship-bottom paints, one of which is the vinyl system.

To cope with the various fouling growths it has been determined that an anti-fouling coating that will leach out a toxic equal to 10 milligrams of copper from a surface 1000 sq. centimeters every 24 hours should be lethal and prevent most attachments. The chemical leaching rate method which was developed at the Navy's Mare Island Paint Laboratory is described in a paper by Ketchum, Ferry and Burns.[5]

SURFACE PREPARATION

One of the most important factors for the successful performance of vinyl protective coatings is surface preparation. Among the various methods for cleaning a surface properly for painting is abrasive blasting. Abrasive blasting will remove old paint, rust, millscale, marine growth, and any other foreign matter. Besides cleaning, blasting produces a rough anchor pattern or profile giving more "tooth" for coatings. According to Burns and Schuh[6] the effective surface for mechanical adhesion is increased by about twenty times per unit area.

ABRASIVES

Military Specifications, MIL-A-21380B (15 July 1965) and MIL-S-22262 (4 December 1959) can be used as basic documents for purchasing blasting abrasives. These specifications identify classes of abrasives and graduation of particle size.

Besides the identification of size of granules, there are requirements as to silica, chloride and moisture content, hardness, free flow and friability properties and specific gravity.

For metals, only an abrasive that leaves a minimum of occluded particles in the blasted surface should be procured, especially when thin coatings are to be applied. Occluded matter is foreign and should not be present for the best coating performance. Besides reducing the effective adhesion surface each mound of occluded abrasive is usually porous, since the occluded material is shattered and extends outward serving as a wick for easy penetration of moisture through relatively thin coating films.

PROFILE

The surface roughness pattern for steel and other structural metals resulting from abrasive blasting is produced by the impact of the abrasive granules against the malleable or distortable surface. The foreign matter on the surface is easily removed and the underlying metal remains essentially intact but pushed aside into hills and valleys. The peak height is the distance from the valley floor to the top of the peak.

When the abrasive leaves the blasting nozzle the large particles because of their greater inertia travel slower than the small particles. There probably is an optimum size granule and shape that produces the greatest roughness in accordance with the impact energy. This energy is given by the formula:

$$K.E. = \tfrac{1}{2} mv^2,$$ where $\underline{m}$ is mass in grams and $\underline{v}$ is velocity in cm/sec.

The resulting degree of roughness is related to the abrasive size, shape, hardness, specific gravity, velocity at impact, friability characteristics and blasting angle. Besides peak height or profile roughness, other identifications such as distribution and shape of peaks and valleys are important.

Figure 3 shows four profiles collectively. A preferred surface roughness compared to a less desirable surface profile is shown by Dietz[8] in the photomicrograph illustration of Figure 4. The less desirable smooth "rolling hill" type of profile was produced with metal shot whereas the preferred roughness showing distinct anchorages was made by an angular abrasive. The optimum peak height depends upon the total thickness of the coating film planned for the surface. A roughness of $1\frac{1}{2}$ - 2 mils is satisfactory for a coating of at least 10 mils. For a coating of only 4-6 mils, a maximum profile is 1 mil or less.

PROFILE MEASUREMENT

The profile can be determined directly with a microscope by measuring the distance from the valley floor to the peak of a number of protrusions. Also utilizing a scaled stage the distribution of peaks can be recorded. This procedure is somewhat arduous and time consuming and is not really necessary since there are instruments that automatically measure profile roughness.

One instrument used to measure average microinch roughness of blasted surfaces is the Brush Electronics Company "Surfindicator", Model BL 110. The microinch values obtained are in accordance with American Standard "Surface Roughness, Waviness and Lay, ASAB46.1-1955 UDC 621.016" or by MIL-STD-10A. Conversion of the average microinches to profile mils is roughly estimated by multiplying RMS (Root Mean Square) values by a "k" factor. This "k" factor may be estimated at unit numbers around 8-10. A RMS value of 200 microinches would be interpreted to mean a maximum profile or peak height of 1.6 - 2.0 mils.

Typical "curves" drawn by the "surfindicator" recorder are shown in Figure 5, showing the four roughness profiles of Figure 3 produced by variable abrasives and blasting air pressures. The top "ups and downs" tracing is the variation of the surface from a set center or zero line, each horizontal chart line on the chart representing 20 microinches for areas 1 and 2 and 40 microinches for areas 3 and 4. The bottom line tracing shows the average values, each horizontal chart line representing 10 microinches for areas 1 and 2 and 20 microinches for areas 3 and 4. There is no question that a surface prepared by abrasive blasting is ideal for painting. However, where the economy or worth of the surface precludes abrasive blasting or that the abrasive would be scattered and possibly damage machinery and equipment, then hand or power chipping, wire brushing, power sanding, scraping, acid cleaning or flame cleaning can be utilized. Old paint can be removed by solvent or water-rinseable paint and varnish removers or alkali chemicals.

Dry blasting with abrasives with high contents of silicious matter can produce high dust and create a health hazard. Also such abrasives usually leave a large amount of occluded particles in the metal which is foreign matter and objectionable for good painting surfaces.

To overcome some of the above deficiencies of certain silicious type abrasives, mineral grit, slag particles or steel shot can be used. It is important to note that steel grit or shot should be used only on steel or cast iron surfaces and not on non-ferrous surfaces. However, such aggregates do not produce the type of roughness conducive to optimum mechanical adhesion.

ABRASIVE WET BLASTING

Dust and occluded abrasive particles can be greatly reduced if wet blasting is used. For wet blasting of steel a rust inhibitor must be included in the abrasive

slurry followed by an inhibitive wash. The inhibitors are not required when blasting aluminum, galvanizing, stainless steel or corrosion resistant alloys. Also inhibitors are not necessary in the slurry if the inhibitor wash-down can be applied immediately after or following the slurry blasting.

The inhibitor slurry is made up as follows:[7]

<table>
<tr><td>4:1 by weight of
diammonium phosphate:
Sodium nitrite</td><td>)
)
)</td><td>2 pounds</td></tr>
<tr><td>Sand</td><td></td><td>300 pounds</td></tr>
<tr><td>Fresh water</td><td></td><td>15 gallons</td></tr>
</table>

The inhibitor solution for washing down the abrasive residue from the blasted area consists of two pounds of the above 4:1 inhibitor salt mix to 40 gallons of fresh water.

PERFORMANCE

In general, coating performances for various degrees of blasted surfaces[10,11] may be estimated as shown in Table I, assuming 100% rating for white metal abrasive blasting and equal thicknesses of coating.

It is obvious that with the very best of surface preparation sufficient coating thickness must be applied to cover the highest profile peaks in addition to sufficient film thickness to serve as a barrier against the destructive environment.

Coating thicknesses of two to three times the average peak height is suggested by Gosse and Cranmer[12] for corrosion protection.

Table II illustrates performance of a vinyl metal primer related to profile and film thickness after exposures in a salt fog cabinet.

Further evaluations have been made by the Mare Island Paint Laboratory relating performance to surface preparation and profile. The following test results are from unpublished paint laboratory data.

A steel panel was sand blasted to give four profiles, identified as Areas 1, 2, 3 and 4. The roughness profiles, in RMS microinches, were previously described and identified by the Figure 5 charts drawn by the Surfindicator. Also photomicrograph shows the respective surfaces in Figure 3. These profiles were: Area 1, 60-70 RMS microinches; Area 2, 100-120; Area 3, 150-190 and Area 4, 200-250. The panel was allowed to remain flat in the laboratory atmosphere for several days after which time rust spots developed, the extent being directly proportional to the surface roughness. This may be explained by the fact that the rougher surfaces had larger "dishes" to condense moisture. Also, these rough surfaces contained occluded porous sand clumps which served as capillaries or wicks to pass the moisture through to the base metal and start corrosion. Figure 6 shows the corrosion spots in the four areas, Area 4 being the roughest and showing the most corrosion.

Another panel was similarly prepared with almost identical profile roughnesses. About 0.5 - 0.7 mils of a white vinyl primer was applied and allowed to dry for 24 hours. The panel was then placed in a salt fog cabinet in a horizontal (flat) position for two days. After this time preferential corrosion resulted

showing increased corrosion with the rougher profile.

Another panel evaluation was made to illustrate the relative merits of a white metal blast versus a sweep blast and corroded surface or no preparation. A steel panel was abrasive blasted and permitted to corrode freely in a salt fog cabinet. Then 1/3 the surface vertically was blasted to white metal, the adjoining 1/3 was cleaned to represent sweep blasting and the remaining 1/3 area was left corroded. Then two thin coats of white vinyl primer were applied leaving a top border of about an inch for future identification of the three surfaces prior to painting. The top of the panel including an additional one inch strip of the painted area, was protected with a polyethylene film. Then the remaining lower part of the panel was placed flat in the salt fog cabinet for about a day. At the end of this time the anticipated preferential corrosion resulted, the untreated rusty coated area showed the most corrosion, the "sweepblasted" area the next high- est and the white metal blasted area showed no corrosion.

Still another steel panel was sand blasted and coated uniformly with a coat of the white vinyl. Then five glass inch-diameter tubes were installed upright on the surface and sealed with paraffin wax. The cylinders then were filled respectively with high purity water, distilled water, tap water, brackish water and sea water. The panel then was placed in an oven at $150^\circ F$ for several days. The permeability relationship between the "five waters" did not follow the sequence anticipated; the most permeable high purity water would penetrate the film first, etc. However, the test did demonstrate that once the waters got through, the most corrosive was sea water. Sea water probably the least permeable of the waters, showed to be the most corrosive environment.

The following panels were prepared to demonstrate adhesion as related to wash primers (Navy Formula #117 olive drab colored, MIL-P-15328, and Experimental Blue Wash Primer, Formula 11S33.) One-half of each panel was coated respectively with #117 and 11S33 and a coat of standard Red lead vinyl Primer, Formula 119, applied over the entire panel. Adhesion of the #119 is poor over bare metal but very good on #117 and #11S33 wash primers. In certain instances, there have been doubts as to whether #117 had been applied to a surface since it cannot be identified once #119 Red lead Primer is applied over it. Some applications may have been deficient be- cause of the lack of the wash primer. With the 11S33 Blue Wash Primer, a prominent blue color is visible.

Another experiment related to adhesion was conducted using overheated #119 Red lead Vinyl Primer. At times irregular blotches of #119 show poor adhesion over #117 wash primer or over previously applied #119. The quick decision would suggest oil or grease on the surface where the #119 would peel. Study revealed that during the hot spray application of the #119, any stoppage in spraying with the heat still on the paint pot could cause local overheating of a mass of #119. This mass would thicken by over polymerizing or the formation of a lead soap with the vinyl resin. The surface over which this blotch of overheated vinyl would be applied would soon lose adhesion and could be pulled off in one large sheet. An equivalent heat of $140^\circ F$ for one hour in a large mass of 10-20 gallons of paint was sufficient to cause this overheating of a portion of the #119. Laboratory experiments were con- ducted simulating overheating. It required about 8 hours at $180^\circ F$ to cause over- heating of a blotch of #119 in a pint volume. It was found that the first coat peeled from the #117 wash primer, the second coat of #119 peeled from the first coat and the third coat peeled from the second. Overheating of #119 in the field was eliminated by setting temperature controls and limiting the maximum temperature to $100-110^\circ F$.

Additional tests were conducted to identify porosity in vinyl films and

determine factors that caused this deficiency and how to eliminate it. At times some evidence of porosity can be detected by observing the surface of the applied vinyl, in this instant, the #119 Red lead Vinyl. Heating the coating causes the air bubbles to expand and become prominent or burst and perforate the coating. Figure 7 shows the many air bubbles on the coating surface and some of which have burst.

Extensive studies were made as to the exact nature of vinyl film porosity caused from air entrapment. Such porous films detract from the impervious proper-ties of vinyls and thus permit water penetration and pinpoint rusting. One ap-proach to the problem was to try to produce vinyl films with excessive air entrap-ment and porosity. The following parameters were explored duplicating the exten-sive work that was done to understand the causes for porous Saran films.

The standard #119 Red lead Vinyl primer contains methyl isobutyl ketone and toluene. Normal spraying, successive cross spray passes with no waiting or inter-val between passes, at ambient conditions usually results in a fairly dense film. This is shown by Figure 8, a photomicrograph of a cross-section of normal sprayed films of the standard orange #119 and a white modification for color contrast, thinned to 60 krebs. It can be seen the films are non-porous.

Changing the solvents in #119 and the white version to solely methyl ethyl ketone, a faster evaporating solvent than the mixture of toluene and methylisobutyl ketone, and observing the same procedure as above (thinning the modified #119 and white to 60 krebs and spraying several passes per coat without a time interval be-tween passes) resulted in vinyl films with some porosity.

Retaining the initial high viscosity of around 70 krebs, no thinning, and ap-plying the orange and white vinyls with MEK single solvent, and spraying in a normal way with cross-passes and no wait or interval between passes, a film with extensive porosity was produced. This is shown by Figure 9.

Again retaining the initial 70 krebs viscosity, using MIBK and toluene sol-vents, spraying with no pass interval a film resulted with a few air bubbles.

Proceeding as in the experiment above but utilizing the pass interval a dense non-porous film resulted.

Modifying the Figure 9 procedure by observing the pass interval a film with only a few pores resulted, showing a vast improvement of the extensively porous film. Figure 10 shows this improved film.

Extreme porosity is caused by utilizing high viscosity orange and white vinyls with MEK fast evaporating single solvent and employing a multiple pass spray procedure without wait or interval between passes.

Table III gives a summary of the various vinyl films discussed and indicates the variable factors of viscosity, solvent, spray procedure and the resulting film characteristic. In conclusion, dense vinyl films can be produced by utilizing a solvent with a relatively slow evaporation rate such as MIBK or slower, by lowering the viscosity, and by observing a wait of 30-60 seconds or interval between spray passes. Brush application, where the air entrapment is practically eliminated, lends itself to producing dense non-porous films in most instances.

SPECIFIC VINYL APPLICATIONS

Solvent vinyls used in the Navy are pretreatment coating, anticorrosives, and antifouling paints applied to the underwater and boottop areas of submarines and surface ships, on steel as well as aluminum and wood. Topside and undersuperstructure surfaces of submarines are finished with vinyl-alkyd solvent camouflage coatings. Solvent Saran coatings were extensively used in fuel and ballast tanks. Their revival is evident with high flash formulations. Latex vinyls are used in polaris submarine interiors to reduce atmospheric contamination which would result from solvent coatings. Certain polyvinyl acetate latexes and preformed tile are used as sound deadening materials such as stopping the drumming of submarine superstructures. Plastisols are used for identification and protection of valve wheels, levers, braces, brackets and tool grip surfaces. These specific applications are summarized.

A. Submarines

	Dry Film Thickness
(1) Keel to waterline at maximum beam (underwater)	
1 coat #117 Pretreatment coating (Wash Primer) MIL-P-15328 (Vinyl used: polyvinyl butyral)	0.5
4 coats #119 Red lead Vinyl Primer MIL-P-15929 (Vinyl used: alcohol modified vinyl chloride-acetate)	6.0
2 coats #121 Red Vinyl Antifouling MIL-P-15931 (Vinyl used: vinyl chloride-acetate)	4.0

(2) Waterline at maximum beam to waterline in maximum condition of diving trim (boottop)

1 coat #117	0.5
4 coats #119	6.0
3 coats #129 Black Vinyl antifouling MIL-P-16189	6.0

(3) Exterior topsides

1 coat #117	0.5
4 coats #119 (or 4 coats $120, MIL-P-15930 for Aluminum) vinyl alkyds	6.0

3 coats #122 Series (Reflectances: 3,7,17,27, etc.)MIL-P-15933
 (Vinyl-alkyd. Vinyl used: alcohol
   modified vinyl chloride-acetate)   through
                            MIL-P-15936
                            etc.
	4.5

(4) Diving Planes

Same as (2)

(5) Rudders and Struts

Sames as (1)

(6) Wood Slat decking

2 coats 122-3 (MIL-P-15933)	3.0

B. Surface Ships

(1) Keel to lower bottopping limit (underwater)

1 coat #117	0.5
4 coats #119 (use #120 for aluminum)	6.0
2 coats #121	4.0

(2) Lower to upper boottopping limit (boottop)

1 coat #117	0.5
4 coats #119 (use #120 for aluminum)	6.0
2 coats #129	4.0

C. Wood Surfaces (underwater)

(1) Keel to lower boottopping limit (underwater)

1 coat #117	0.5
2 coats #121	4.0

(2) Lower to upper boottopping limit (boottop)

1 coat #117	0.5
3 coats #129	6.0

To attain the above proper thicknesses, review the wet film - dry film relations as summarized in Table IV, along with expected spreading rate in Table V for the various coatings.

D. Sonar Domes

Of special importance is the vinyl coating system on stainless steel sonar domes. The absence of any coating will invite fouling attachments and subsequent perforations in some instances through the metal (particularly thin gage stainless steel) because of the creation of oxygen-concentration cells. Also marine growth protrusions promote noise, rendering the sonar inefficient for critical sound detection. The use of a porous coating absorbs sound energy and causes attenuation. Blistering or peeling eventually cause noise by loose paint vibrating in the water stream while the ship is underway. The only practical means of protection of sonar domes is a cover of a smooth, adherent, tough non-porous antifouling coating system. The vinyl shipbottom coatings with certain application modifications such as heat drying between coats have performed in an excellent manner on certain sonar domes.

For 100 inch and 185" stainless steel sonar domes the following specific surface preparation and coating procedures are followed.[7]

1. Remove any grease and oil using emulsifying-type cleaner followed by hot-water rinse. Pressure wet blast, using a slurry of abrasive and water. (Dry blasting results in embedding particles of abrasive into the "CRES".)

2. Wet blast at 40-60 pounds air pressure with an abrasive slurry containing 110-120 mesh silica sand and water. A

suitable ratio of sand to water is one gallon dry sand to three gallons of water. (The resulting finish should have a roughness of 75-125 microinches as identified by the American Standard "Surface Roughness, Waviness and Lay, ASA B46. 1-1955 UDC 621.016" or by "MIL-STD-10A" of 13 October 1955 (slightly rougher surface is acceptable). A finish of 75 to 125 microinches is commonly known as a satin finish. An instrument that can measure the roughness of the sandblasted surface is the Brush Electronics Company "Surfindicator" Model BL 110. A close inspection of the blasted surface must be made to insure that holidays are detected and reblasted. The final finish should be uniform white metal.

3. After blasting, the surface shall not be touched and foreign matter shall not be allowed to come in contact with the surface. All exterior surfaces should be covered (clean paper is suitable) when dome is transferred to another location. Do not use masking tape directly on blasted surface. All painting shall be accomplished under shop conditions in a clean atmosphere and a temperature of at least 60°F. When dome is ready, paint immediately.

4. Apply one coat (in two crossed-spray passes) of Formula #117 to obtain a dry-film thickness of approximately 0.7 mils. The surface shall be dried under mild heat, such as lamps, at a surface temperature of 100°F. to 110°F. Spray apply Formula 120 to a dry-film thickness of 1.5 mils and permit one-hour drying at 100°F. to 110°F. Spray apply Formula #119 at 1.5 mils dry-film thickness and repeat drying. Spray apply a second coat of Formula #120 and Formula #119 at a dry-film thickness of 1.5 mils each and repeat drying procedure. Then spray apply two coats of Formula #121 to a dry-film thickness of 2 mils each and allow drying at 100°F to 110°F. between coats. Allow final coat to air dry for a minimum of four hours before handling. The complete system should have a minimum dry-film thickness of 10.7 mils.

5. Where painting of the mounting, fairing strips, and hull area within five feet of the mounting is required, the foregoing vinyl system should be applied. If painted dome is more than three months old prior to installation, apply 1 coat of Formula #121.

6. The foregoing method is applicable for CRES domes. For non-CRES domes, dry or wet blast may be used. Although the heat drying procedure is not required, care should be taken to ensure release of solvent between application of coats. Heat however, is the best way to assure that the solvent is released.

Although the above vinyl coating system has performed satisfactorily on CRES sonar domes certain wear patterns due to the sonar energy are evident after about two years. This wear is not critical but steps are being taken to try to eliminate this deficiency.

Figure 11 shows the typical wear pattern of the vinyl sonar dome paint system

on the Isherwood after two years of successful operation. The wear patterns do not go beyond the #119 or #120 vinyl anticorrosives.

Efforts to use this vinyl coating system in the "powerful" SQS-26 sonar dome were not too successful since the wear pattern was accelerated many fold. A solution was found, however, which utilizes the vinyl undercoat system with a topcoat system of neoprene rubber (Gaco N-29) and the polyisobutylene Navy standard antifoulding paint for rubbers, Formular #134, MIL-P-22299. Because of the rubbery nature of the neoprene and #134 A.F., the sonar wear has been satisfactorily reduced.

Laboratory evaluations have been made of various coating systems by subjecting coated panels to sonar energy. A comparison was made evaluating the all-vinyl system with the vinyl-neoprene-polyisobutylene system.

Figure 12 shows the cross-section of the vinyl-neoprene-polyisobutylene SQS-26 sonar dome coating system, along with stretched films to show elongation effects which are related to sonar wear resistance. It will be noted that the 134 and neoprene stretched successfully whereas the #119 cracked. Since the wear action hardly ever reaches the #119 vinyl, its presence as a good anticorrosive enhances the paint system.

FUEL AND BALLAST TANKS

Some years ago, the Navy formulated a very successful tank coating known as Saran, Formula #113 (MIL-L-18389), based on the copolymer, vinylidene-chloride-acrylonitrile. The initial brush applications resulted in dense non-porous films and showed excellent corrosion protection for several years having been subjected to aviation gasoline and sea water. Then, due to an economy move, Saran was applied by spray. Many of these sprayed jobs showed premature pinpoint rusting such that early paint repairs had to be made involving considerable expenditures. The real reason for these early failures was not recognized until studies were made of the spray applied Saran films. Film cross-sections were viewed through the microscope and the picture that was seen was quite alarming. Figure 13 is a cross-section of Saran taken from a submarine tank. It can be understood the reason for early pinpoint rusting. It was anticipated that porosity or bubbles in the dry Saran film could only be formed by air entrapment. The process was similar to the effect of dropping a stone in a pond. Air bubbles may be seen following the stone down and then returning to the surface to break and disappear. Similarly, if there is a wet film of Saran on a surface (the pond) and an additional spray coat or pass is immediately applied, the atomized droplets of Saran (the rock) carry air with them when they strike the applied Saran and cause the air to penetrate into the wet film. Before the bubbles of entrapped air can return to the surface of the Saran to escape, a membrane or skin forms at the surface because of the fast evaporation of the methyl ethyl ketone solvent. The air bubbles cannot escape through this membrane and remain in the film to produce porosity. Each spray coat or spary pass builds up an additional layer of pores.

If the Saran film, or films of any of the high linear vinyl polymers, is to be dense, without air bubbles, the air that is carried in with the paint droplets as the spraying is continuing must have time to escape before the skin or membrane forms on the surface of the Saran. Because Standard #113 Saran (MEK Solvent) will dry or skin-over rapidly, any air within the applied film has only a short time during which to travel outward toward the surface of the coating in an effort to escape. To permit the air to escape so that a dense non-porous film can result,

it is required that the distance or the thickness of the wet paint be limited. A thin wet film of Formula #113 will permit most of the air to escape, whereas a thick film will keep the air entrapped. The single spray pass of standard Saran is too thick to permit all of the entrapped air to escape. Also, because of the fast evaporation of the methyl ethyl ketone solvent, the viscosity of the applied fluid Saran is high almost at the instant the material reaches the surface.

By thinning the Saran and applying a single pass with a minimum of overlap, the applied coating is thin enough and the viscosity low enough to permit mobility of the entered air and its exit before the formation of a skin or high internal viscosity. About 30-60 seconds wait or pass interval is required between spray passes to assure a dense non-porous Saran film.

By using a slower evaporating solvent, such as cyclohexanone, methyl isoamyl ketone or pentoxone and a diluent like 1 - nitropropane, high flash safety solvent Saran coatings are formulated that lend themselves to normal spray applications without porosity. Because of the slower evaporating solvents, the applied film remains at a low viscosity long enough to permit air bubbles to escape before the surface membrane forms. These spray techniques were used to produce the dense vinyl films discussed earlier.

PLASTISOL VINYL COATINGS

The plastisol type coating, consisting of polyvinyl chloride resin and a plasticizer or mixture of plasticizers and pigments has found widespread use in the Navy for coating metallic objects to provide corrosion protection and to impart a comfortable feel. The usual application is 1/16" to 1/8" which has good resistance to abrasion and to immersion in moderate concentrations of acids and alkalis at temperatures below 140°F. Such coatings can stand occasional cleaning and splashing with detergent solutions, organic solvents and petroleum based fuels and lubricants. However, continuous immersion in these liquids is not recommended.

The application of plastisol is summarized under the current specification MIL-P-20689A. The usual procedure is to clean the metallic object and sometimes roughen or chemically treat it; to apply and cure, usually by baking, the primer; to heat the primed object to a suitable temperature and to immerse the heated object into the plastisol (or to apply the plastisol by spraying.) A jell coating of the plastisol will adhere to the surface. The thickness of this coating can be controlled by varying the temperature of the part before immersion, the immersion time, the rate of withdrawal from the bath and the number of dips. Then the coating is fused by heating the coated object for the proper time and the recommended fusing temperature usually 350-400°F.

Under MIL-P-20689A there are two types and two classes under each type as follows:

        Type I - General purpose dipping compound
                Class 1 - General use
                Class 2 - Fungus resistant use

        Type II - Chemical resistant compound
                Class 1 - Dipping
                Class 2 - Spraying

This specification covers black only unless other colors are specified. The color match shall be based on the final fused material.

Navy standard Plastisol colors and color coding was reviewed by the Materials Testing Laboratory of the Portsmouth Naval Shipyard.

VINYLS IN CATHODIC PROTECTION

Because of their resistance to alkali, certain vinyl coatings have shown good performance when used in combination with cathodic protection. Deficiencies that may have developed at times can probably be traced to application faults resulting in porous films, films not of the proper thickness, etc. Although certain coal tar epoxies may also show effective performances around anodes in cathodic protection systems, well applied vinyls can still do a job.

An important phase of cathodic protection may involve the use of top coated zinc rich coatings on underwater surfaces. At the present time successful applications of vinyls over certain inorganic zinc coatings have been made to boottop areas. The system consisted of #117 wash primer (MIL-P-15328) #119 Red lead vinyl and #129 Black vinyl antifouling paint. The use of #117 to promote adhesion appears to follow the same good results as the use of the pretreatment coating (wash primer) on galvanizing. Also, a good parallel is the improvement of adhesion on galvanizing if the surface is roughened mechanically. Although no special efforts have been made to mechanically roughen inorganic zinc coatings, certain formulations have been made that develop a desired roughness profile during application and drying or curing.

Extensive laboratory tests have been made on zinc rich coatings of which certain tests have been designed to evaluate the cathodic protection properties. One such method described by Saroyan[13] and first utilized by Munger[14] makes use of "V" holiday or bare area on a panel with the adjacent areas coated with the zinc coating. The effectiveness of the coating is interpreted by the degree of protection it offers. Usually the wide part of the "V" starts corroding first since certain zinc coatings do not have the "throwing power" to protect distant surfaces. The apex or tip of the "V" usually is the last spot to corrode. The Figure 14 photograph shows three such test panels of varying cathodic protection effectiveness. In addition to the main purpose of the test, that of evaluating cathodic protection properties, certain adhesion studies of top coats are also included. One of the adjacent areas, the left in this instance, was coated with #117 wash primer and the bottom half further coated with one coat of #119 Red lead vinyl. The panel was then immersed in sea water or brackish water and, the various performances noted and graded at specified intervals. As can be seen, although panel Number 1 shows good cathodic protection, there is some loss of adhesion of the #117 over the zinc rich coating, with some blistering of the #119 on the lower half. Through such evaluations, effective coating systems are found which show promise as cathodic protection coatings for underwater use. Certain zinc rich coatings top coated with vinyls have shown to be very effective underwater systems.

VINYLS FOR SUBMARINE TOPSIDE

Some degree of success has been established for vinyls as a topside coating for submarines. Although at the present time, there are indications that certain chemical coatings like the epoxies and coal tar epoxies, do contribute to corrosion protection, chalking and loss of initial gloss leaves a measure of performance yet to be attained.

The vinyl topside system consisting of #117, #119 and #122 series (vinyl-alkyds) lends itself to drying in cold weather whereas chemical coatings (epoxies,

etc.) require temperatures above 50°F to cure properly.

Although the film guild-up with vinyls is slow, perhaps non-porous dense vinyl films applied at minimum film thicknesses can make up for total thickness now required.

Touch-up painting of the vinyl-alkyd camouflage coatings has presented an adhesion problem. In some instances decorative or cosmetic coats of vinyl-alkyds applied over aged coatings lose adhesion in a few months. The exact nature of this deficiency has not been established, but indications are that a surface layer of highly polymerized paint exists which solvents from the newly applied coating do not solvate and hence a layering or peeling appears in time. The removal of this layer by sand washing or utilizing potent solvents in the touch-up paint, appears to improve this deficiency.

Another approach to this problem is to formulate with high flash solvents which can permit solvating old aged vinyl-alkyd paint. Although vinyl-alkyds show fair performances as decorative coatings, an improvement is expected by modifying the formulation to include vinyl-silicone alkyds.

LATEX VINYLS FOR SUBMARINE INTERIORS

Standard interior finish paints for Navy ships is a chlorinated alkyd base coating which is fire retardant. For submarines, particularly the Polaris type, however, certain precautions have to be taken in using solvent coatings since residual solvents will slowly be released to the atmosphere and cause serious contamination that carbon dioxide scrubbers cannot efficiently trap or "burn up". Such solvent base paints are safe to use on interior surfaces up to 5 days prior to departure to sea. After this time, when a fair amount of painting still has to be done, the following latex or water base paints which are believed to be vinyls have been approved for use:

Amercoat 1768	Amercoat Corp.
Deflex MD 2707	Devoe & Raynolds
Ocean 634	Ocean Chemicals

Also, surfaces that are lined with elastomeric foamed plastics insulation (MIL-P-15280) should be coated with one of the above latex interior paints since solvents from solvent based paints are readily trapped in the foam material and not released as fast as required.

PERFORMANCES OF VINYL SHIPBOTTOM PAINTS

The vinyl shipbottom paints have shown good performance records and compare favorably with the notorious hot plastics shipbottom paint system.

Certain comparative service test dates were presented at "The Second Inter-Naval Corrosion Conference" in Sidney, Australia, 22-26 November 1965, under the title of "Control of Ship Fouling in U. S. Navy".

During the early evaluation period 57 ships (exclusive of submarines) received vinyl bottom paints in 1951 and 1952. These included 10 destroyers quarter painted with vinyl and hot plastics, 32 surface ships (besides destroyers) quarter painted with vinyl and hot plastics and 15 destroyers completely painted with vinyls (five of which were compared with destroyers in the same division coated with hot plastics).

The test results showed the following:

1. The vinyl paint system was slightly better than the hot plastics system with respect to corrosion resistance.

2. The vinyl and hot plastics systems were about equal with respect to fouling resistance, except in certain instances in tropical waters where vinyls fouled.

3. A substantial number of ships showed no difference in performance between vinyl and hot plastics systems.

4. The service performance data on active ships showed that the two paints performed equally well in all respects and that any choice between them has to be based on other considerations. These include:

A. Frictional Resistance

The vinyl system was between four and nine per cent better than the hot plastics system "fresh out of dock". With increasing time out, the vinyl system lost its advantage. At 22 months, the two systems required about the same horsepower to maintain certain speeds. The average advantage of the vinyl system over the hot plastics system was 2-5%. Reduction in power resulted in a small increase in maximum speed and reduction in fuel consumption. Because of this speed advantage, the vinyls were adopted for destroyers at an early stage. Today, vinyls are used exclusively on submarines and on some surface ships.

B. Cost

The cost of vinyls is a little more than for the hot plastics because 7 coats of paint are required vs. 5 coats for the hot plastics system.

APPLICATION

Special equipment is required for hot plastics but the normal vinyl applications are done with conventional spray equipment. However, in order to gain film buildup, reformulations have been made in the vinyl formulations to allow advantageous applications with airless or hot spray equipment. As previously illustrated, the vinyls should not be overheated since an adhesion problem can result.

SURFACE PREPARATION

Adequate surface preparation is necessary for both vinyl and hot plastics systems. However, surface preparation is more critical for vinyls.

FILM THICKNESS

The vinyl requires seven coats to obtain a total film thickness of around 10 mils dry film. Insufficient film thick results in blistering and ultimate failure of the coating. Porosity may also contribute to early failure. Hot plastics usually is applied at 30-35 mils, the undercoats being around 3-4 mils.

DRYING TIME

Under good weather conditions the entire vinyl system can be applied in a
day. However, care must be taken to avoid solvent and air entrapment which can
promote blistering.

REPAINTING

Repainting was supposed to be one of the assets of the vinyl shipbottom
paint system. This has only been borne out in part perhaps because of the lack of
total knowledge how best to do a repainting or touch-up job. Some successful
touch-up vinyl shipbottom paint applications have extended the total performance
period of the initial application to around 3 years.

PERFORMANCE UNDER CATHODIC PROTECTION

Because of their inertness to alkali, as previously indicated, vinyl coatings
are suited for application on ships with cathodic protection where an alkaline
medium is generated. This is a strong argument for the use of vinyls on shipbottoms
especially when consideration is being given to use cathodic protection on all new
construction ships.

SHIP PERFORMANCES

Current performances of vinyls on submarine shipbottoms has been very good,
especially the fouling resistance of the 121 (Red) Vinyl A.F. The black #129 vinyl
used on the diving planes and at the bottop area, has not performed as well.

Figure 15 shows the condition of the vinyl shipbottom paint on the USS MEDRE-
GAL after being in service for 8 months. This same good performance was recently
noted on the USS POMODON after 14 months of service.

FUTURE USE OF VINYLS IN THE U. S. NAVY

A. Shipbottom

    At the present time underwater surfaces of most submarines are
    coated with the vinyl system 117-119-121. Certain surface ships
    also use the vinyl shipbottom system. On the basis of permanent
    anticorrosives, certain epoxy coatings appear to lend themselves
    to good performance and repairs at interim dockings. These
    epoxies may compete favorably on the basis that three coats of
    paint need to be applied to obtain the 8 mils of anticorrosive
    desired, whereas five coats of the present vinyls (1-117, 4-119)
    have to be applied to get the 6 mils required. On material cost
    basis, the vinyls are not as costly as the epoxies. Both vinyls
    and epoxies can be applied with standard spray equipment. The
    safety precautions for the present vinyls are more demanding than
    the epoxies. The #121 vinyl antifouling paint is more efficient than
    any of the epoxy A.F.s. The future outlook for vinyls on shipbottoms
    may be summarized as follows:

1. Vinyl antifouling paint #121 (MIL-P-15931) will continue
    to be the Navy Standard. Probably a high flash formulation
    will supersede the present low flash paint.

2. Assuming the use of cathodic protection vinyl anticorrosives
    will still be considered in competition with epoxies or coal
    tar epoxies. Dense, non-porous vinyl A.C.s will invite
    their use in view that fewer coats can be applied. High
    flash compositions will eliminate the present hazards and ex-
    pense of safety precautions.

3. With inorganic zinc coatings as a possible universal primer
    including shipbottoms, the vinyl system with the #117 wash
    primer as the tie coat looks very promising.

4. The vinyls will definitely show an advantage during cold
    weather, below 50^OF, when chemical coatings cure slower.

B. Rudders, Struts, Sonar Domes (Cavitation-erosion areas)

Vinyl coatings have not performed satisfactorily on severe cavitation-
erosion areas such as certain rudders, struts and sonar domes. Vinyls
have served as undercoats, but rubber-like topcoats have to be in-
stalled in order to resist the destructive actions. However, for low
speed ships, the standard vinyl shipbottom paint system is acceptable.

The outlook is that vinyls will be used on rudders and struts for slow
ships and 100" and 180" stainless steel sonar domes.

C. Boottop Areas

Successful applications of vinyls have been made to boottop areas
especially in combination with inorganic zinc coatings. The one de-
ficiency has been the unsatisfactory performance of the black anti-
fouling paint, Formula #129. The accumulation of green algae and
some calcareous growth has detracted from appearance and also has
caused some damage to the topcoats. However, efforts are directed to
develop a more satisfactory black A.F.

It appears that vinyls will continue to be used at the boottop areas
in systems with zinc rich coatings. There will be competition from
epoxies, coal tar epoxies and some rubber coatings.

D. Topside

The problem of recoating aged vinyl-alkys where peeling and loss of
adhesion appears, has been the reason to look to other coatings such
as epoxies. Although epoxies appear to give good corrosion protection,
however, even with epoxies, recoating of aged paint may still present
an adhesion problem. At the present, isophorone solvent is added to
the touch-up or cosmetic coat of vinyl-alkyd. For improving adhesion
of epoxies over aged epoxies, dimethyl formamide is added to the
touch-up paint. An overall improvement in adhesion is promoted by a
sand-wash of the surface before applying a new coat of topside paint.

Again, because of slow curing of epoxies at temperatures below 50^OF,

the vinyls and vinyl-alkyds may well be kept in the system as a military requirement. Also, with reformulation using high flash solvents, solvating or "biting into" old vinyl-alkyd may well solve the recoating problem.

E. Tanks

Although the inorganic zincs, epoxies, coal tar epoxies and urethane coatings have shown excellent performances in tanks, still the improvements in Saran to produce nonporous dense films may usher in a new era for this vinyl coating. Also, with the first coat enriched with zinc dust to promote some cathodic protection, Saran could be an efficient and economical coating for tanks.

F. Interiors

The present yellowing problem with chlorinated alkyd fire retardant interior paints and the requirement in certain submarines not to use solvent base paint five days prior to departure, opens the way for increased vinyl latex paints for more extensive interior use for Navy ships.

G. Sound Insulation

Vinyl latex and vinyl based tile or blocks will continue to be used for sound damping and eliminating noise on ships as a military requirement.

H. Decks

Vinyl tile will continue to be used as a decorative and utility type of covering for interior decks.

I. Plastisol

Plastisol will continue to be used for application on metal items such as valve wheels, levers and tool grip areas.

CONCLUSION

For the next five years at least, it seems that the Navy will continue to use certain vinyl coatings as outlined. The efforts of supervision to produce dense nonporous films applied at proper thicknesses will certainly help the choice for vinyls. The reformulation to use high flash solvents will remove the hazards and release some of the costly safety precautions. Vinyls have won a place in the Navy and their uses should continue for quite some time.

PHOTO CREDITS

All photographs in this paper are "Official U. S. Navy Photographs".

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TABLE I

EXPECTED PERFORMANCE OF COATINGS RELATED TO SURFACE PREPARATION

Type of Blasting	Effectiveness: Coating Protection, %*
White metal	100
Commercial blast	80 - 60
Sweep blast	60 - 50

*These values are based on the vinyl shipbottom paint system lasting about 36 months when applied over "white metal". Touch-ups which utilize sweep blasting coat about 18 months or about 50% of the original "white blast".

- -

TABLE II

PERFORMANCE RELATED TO PROFILE AND COATING THICKNESS

Panel Profile, mils	Paint Thickness, mils	Salt Fog Cabinet Test Results		
		7 days	35 days	102 days
1.8	1.6	Few rust spots	Additional rust spots	Scattered pinpoint rust spots
1.8	3.8	No change	No change	Few tiny rust spots
1.8	5.7	No change	No change	No change

The test results show that thin films of one profile thickness leave peaks unprotected and prone to early pinpoint rusting. The two profile thickness of vinyl gave fair protection while the three profile gave excellent corrosion protection.
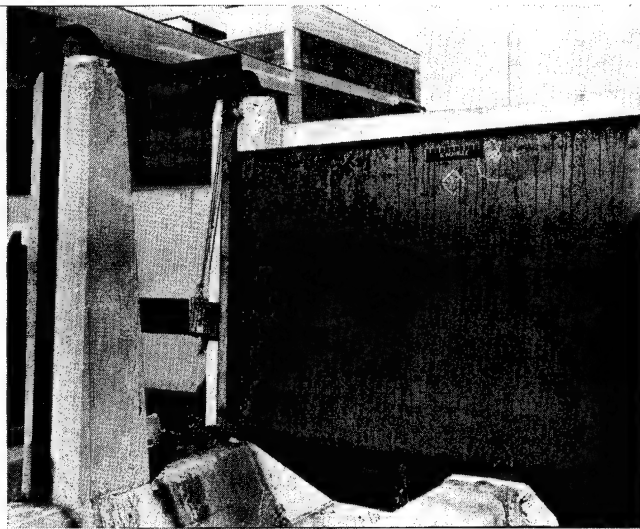
TABLE III

STUDY OF VINYL FILM POROSITY

Figure No. Photomicrograph	Solvent	Viscosity, KREBS	Coats	Thickness, mils	Spray Procedure	Nature of Film
Slide 4	MIBK	60	5	12	No interval	Dense
Slide 3	MIBK	60	5	35	No interval	Dense
Slide 1	MEK	60	3	15	No interval	Few pores
Slide 2	MEK	60	3	25	No interval	Few pores
Slide 6	MEK	70	5	40	No interval	Many scattered pores
Slide 7	MIBK	70	3	12	No interval	Few pores
Slide 8	MIBK	70	5	10	Interval	Dense
Slide 9	MEK	70	5	12	Interval	Few pores
Slide 5	MEK	70	5	40	No interval	Many large pores

TABLE IV

DRY FILM THICKNESSES RELATED TO WET FILM (MILS)

Trial	Paint	Spray Passes	Wet Film, Mils	Dry Film 18 hrs. dry, Mils	% Dry Film of Wet Film
(1)	117	2	2.2	0.5	23
(2)	117	2	2.1	0.5	24
(3)	119	2	2.0	0.5	25
(4)	119	2	2.2	0.6	27
(5)	119	2	2.0	0.5	25
(6)	121	2	3.0	1.5	50
(7)	121	3	3.9	1.8	46

TABLE V

THICKNESS AND SPREADING RATES (DRY FILMS)

Coating	Thickness Per Coat, Mils	Spreading Rate Per Gallon At Indicated Thickness	
		Sq. Ft.	Mils
117	0.5	250	0.5
119	1.5	35	6.0
121 or 129	2.0	125	4.0
122 Series	1.5	100	4.0

FIGURE 1: Corrosion in action. Corrosion in ship-
building starts at the plate rack because
of the millscale which is cathodic to the
iron under it. If the millscale is not re-
moved, corrosion will continue causing
deep pits and eventual perforations.
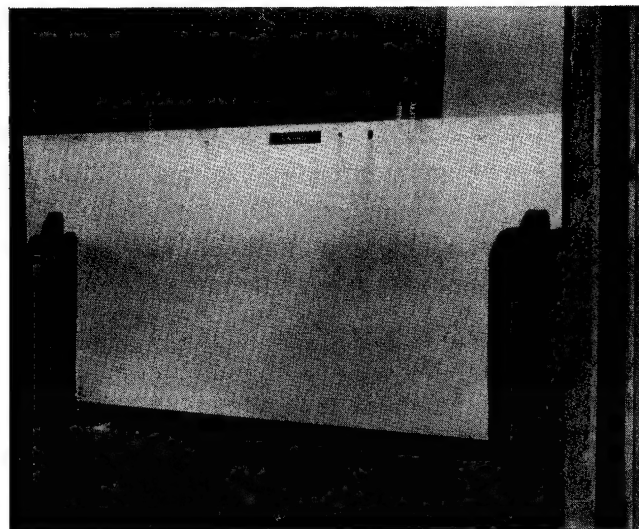
FIGURE 2: Millscale removed from the steel plate by
abrasive blasting and painted with a shop
or construction primer. Formula 84, zinc
chromatealkyd base paint. The first step
in preventing corrosion in shipbuilding
(removing the millscale) has been accom-
plished.
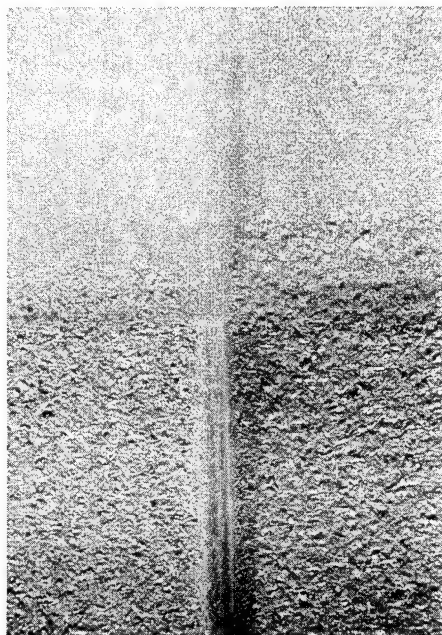
FIGURE 3: Composite of the four surfaces showing
the comparative roughness profiles. In-
cluded is an area of polished metal as a
visual control.

SHOP UNDERSTANDING OF GOOD SURFACE PREPARATION

PHOTOMICROGRAPHS OF BLASTED STEEL
ILLUSTRATING SURFACES
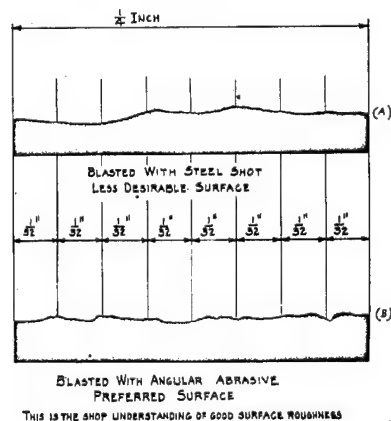
FIGURE 4: The less desirable smooth "rolling hill"
type of profile produced by shot as com-
pared to the preferred roughness showing
distinct anchorages as made by an angu-
lar abrasive.
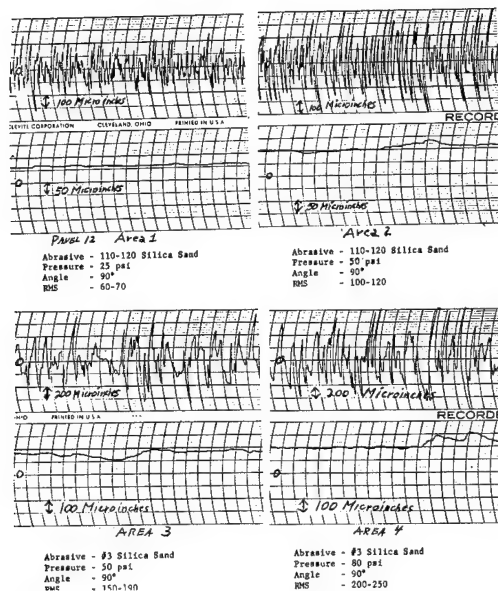
FIGURE 5: RMS (Root Mean Square) type profile chart as drawn by "Surfindicator." Values are in microinches. Maximum peak heights in mils (distance from valley floor to top of peaks) is equal to about 8-10 times the RMS values. Average peak heights is about 4-5 times RMS values.
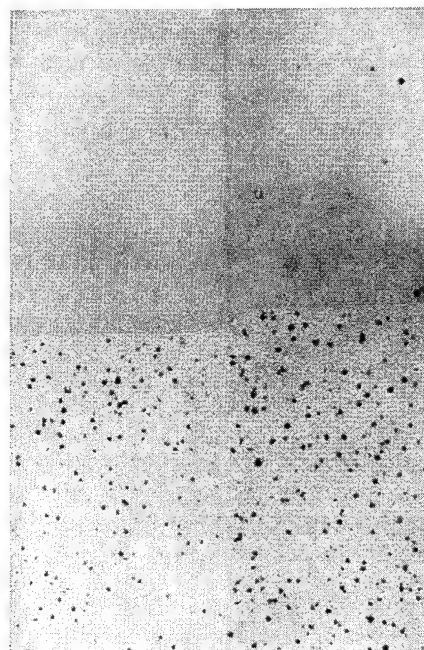
FIGURE 6: Preferential atmospheric corrosion of plasted surfaces of varying profiles. The roughest area, No. 4, has greater moisture condensing surface and occuled sand to promote maximum corrosion.

FIGURE 7: The #119 heated to release the entrapped air, showing more prominent air bubbles and some that ruptured to form craters down to the metal surface.
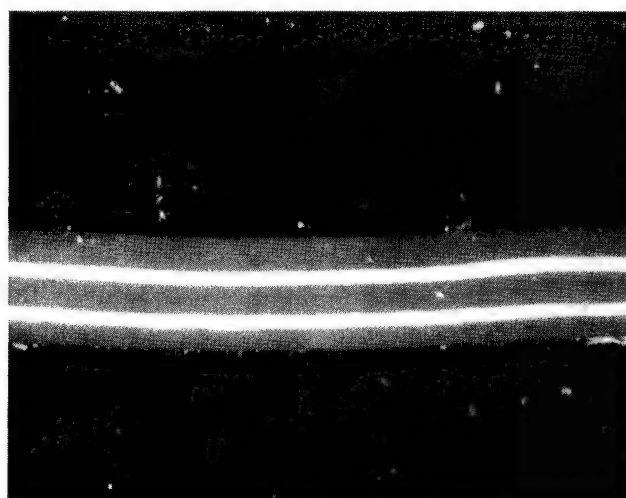
FIGURE 8: Non-porous vinyl film cross-section with 5 coats at 35 mils.

FIGURE 9: Cross-section of vinyl film showing excessive porosity resulting from high viscosity paint (70 krebs) and fast evaporating MEK solvent. The spraying was done in multiple cross-spray passes without any time interval between coats.
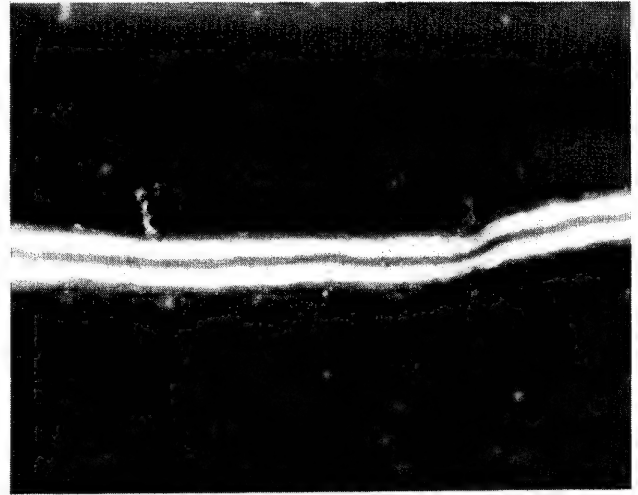
·FIGURE 10: Cross-section of vinyl film showing reduced porosity over the film of Figure 9 by utilizing the pass-interval spray application technique, with all other variables held constant.
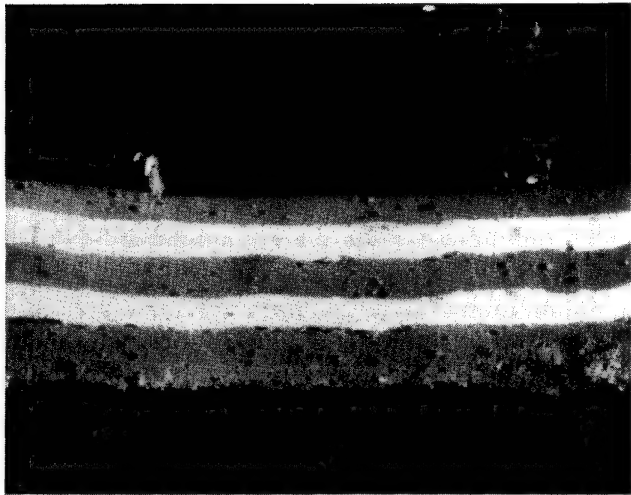

FIGURE 11: Typical wear of the vinyl coating on the stainless steel sonar dome on the USS ISHERWOOD after 2 years of service. The wear is only down to vinyl primer.
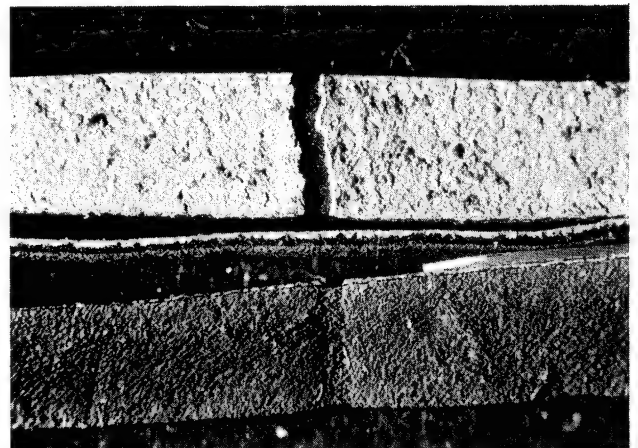
FIGURE 12: Photomicrograph of the cross-section of the vinyl-neoprene-polyisobutylene sonar resistant coating system along with stretched films to show elongation effects as related to sonar wear resistance. The neoprene and polyisobutylene coatings stretch and resist sonar energy, while the #119 cracks and can be worn down by "high powered" sonars.

FIGURE 13: Photomicrograph of the cross-section of a Saran film taken from a submarine tank. The same type of porosity is present as indicated for normal spraying.
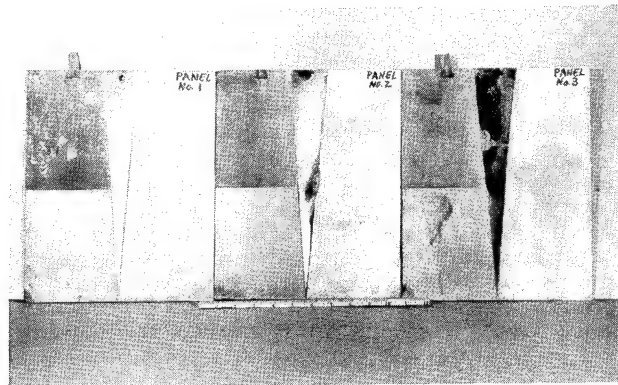
FIGURE 14: Cathodic protection evaluation test panels with the "V" holiday bare steel area, showing degrees of protection of inorganic zinc coatings. #117 wash primer and #119 red lead vinyl are evaluated also as a top coat system.
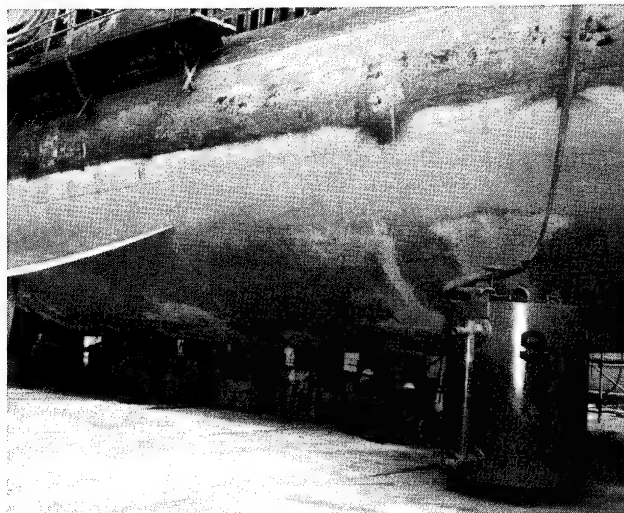
FIGURE 15: Vinyl shipbottom paint system on the USS MEDREGAL, starboard side amidship, after 8 months service.

TESTING METHODS FOR OBTAINING RHEOLOGICAL

AND GELATION MEASUREMENTS OF PLASTISOLS

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Characterization of the flow and gelation properties of vinyl plastisols has been the subject of many recent publications. The fact that there are many methods of obtaining this type of data is evidence that the properties being investigated are somewhat elusive and often different techniques result in different estimates of these parameters -- all of which cannot be accurate.

This paper describes two test methods used by our laboratory which have been proven adequate to define the properties being tested. Generally speaking, these tests do not employ new techniques, but are interpretation attempts to apply theoretical knowledge available to the industry. Since the type of measurements involved are of the physical nature, we must, therefore, use mathematics to describe and interpret our results. Fortunately, in today's modern world, we have many tools available at our fingertips which greatly reduce the amount of effort required to obtain the desired results.

VISCOSITY MEASUREMENTS AT LOW SHEAR RATES

A rotational viscosimeter, such as the Brookfield, is widely used by the plastisol laboratories and, with proper interpretation of the data it produces, is a very satisfactory instrument. (Basically, it consists of a motor, spring, variable speed drive and spindle. The motor rotates the spindle, or bob, in the liquid whose viscosity is being measured, and the drag of the liquid on the bob is read as a deflection on a spring. The degree of deflection is obtained as a scale reading and represents a torque measurement.) With this instrument, viscosity is calculated from the indicated torque, or scale reading, and is multiplied by a factor that depends on RPM and the spindle geometry.

The main problem with the normal approach to viscosity measurement stems from the fact that the commonly-used spindle is a disc, and as such, the torque generated is of a complicated nature. In the case of a Newtonian liquid where the rate of shear changes uniformly with shear rate, the spindle may be accurately calibrated. However, since plastisols often have complicated rheology, the geometric problem becomes very serious. Using a cylindrical spindle, where the "disc-like" ends are small compared to the sides, the sides are a constant distance from the axis and have a uniform peripheral velocity.

The rheological behavior of a material is the result of many individual parameters, all of which contribute to the flow properties. Therefore, it is necessary to measure each one of these parameters separately (if possible) if one is to thoroughly understand a system. Let us first discuss our method for making these measurements and then the way we manipulate the data.

The plastisol, of which the viscosity is to be measured, is conditioned in a one-pint can at 25°C in a constant temperature bath. Temperature is very important in that we have observed up to a 5% error due to a variation of just 1ºC from the specified temperature. The size of the container is also very important because some instruments are designed for an infinite sea – and the smaller the container, the greater the correction to the shear rate. The one-pint can, when used with either the LV-2 or the LV-3 Brookfield spindle, is large enough to avoid complication.

After conditioning, the spindle is inserted into the plastisol, attached to the viscosimeter, and the viscosimeter is turned on at 20 RPM. Scale readings are obtained at this speed after 1, 2, 4 and 8 minutes without stopping the instrument (this is easily accomplished with a little practice). Immediately after obtaining the 8-minute reading, the instrument is shifted to the next lowest RPM available and read as fast as possible without stopping the machine. This procedure is continued to the lowest possible speed. These scale readings represent the raw data that is used for determining the viscosity parameters. The first series of readings at 20 RPM are used to determine the thixotropic breakdown coefficient (B) which relates to the rate of breakdown to the shearing time at a given shear rate. If all of these values are the same, there is no thixotropic breakdown. However, if there is a significant reduction in the scale reading, the material exhibits thixotropic properties, and a plot of the logarithms of the scale readings versus time will show a linear relationship. The thixotropic index (B), which represents the slope of this line at a given shear rate, can be calculated using the following equation:

$$B = \frac{S_a - S_b}{\ln \left(\frac{b}{a}\right)} F$$

Where S_a is the scale reading at a minutes and S_b is the reading at b minutes. In our case, a and b are 1 and 8 minutes. F is a factor for the particular spindle and speed used, and ln is the natural logarithm of the ratio of the observation times. In this equation, it has been assumed that there has been little change in yield value.

The remainder of the data is plotted on rectangular coordinants using scale readings as ordinant and RPM as abscissa. The data, when so plotted, will form any one of many types of relationships as shown on Figure 1. The simplest type of flow properties is exhibited by Line No. 1 on this figure. It is characteristic of Newtonian flow. It indicates that a simple linear relationship exists between the stress and the rate of strain or shear rate. The next most complicated system is shown by Line No. 2 where a similar linear relationship exists except the line does not pass through the origin, but is displaced by some value which is represented by Y_i in this figure. This type of flow is called Bingham. Y_i is related to the yield value and represents the force that must be overcome before the liquid will flow. When such a relationship is found, the actual yield value in dynes per square centimeter can be obtained using the following equation:

$$Y = Y_i \ f_y$$

Where Y_i is the intercept on the scale reading axis, and f_y is the yield value factor for the spindle used. Tables for the f_y factor are contained in the Appendix to this paper for the various cylindrical spindles.

The third line, which is curved, represents a more complicated system. If this line is concave on the lower side, the material is pseudoplastic; if the curvature is concave upwards, it represents the dilatant case. Curved lines are difficult to study; we, therefore, replot the data on log-log graph paper. The procedure for handling this type of material is to estimate the yield value, or Y_i, and then subtract this value from all the scale readings at the various RPMs. This data is then plotted on log-log paper using RPM as the abscissa. This usually produces a straight line or a very nearly straight line - a curved line implies that our estimate of the yield intercept was incorrect and needs adjustment. Once a straight line is obtained, we measure the angle the line makes with the RPM axis with a protractor.

It is important to note that if the above procedure had been used with Lines Nos. 1 and 2 of Figure 1, a straight line would have been found on log-log paper and these lines would form an angle of 45 degrees; whereas in the case of Line No. 3, the angle will be less than 45 degrees. For example, if a line with a slope of $40°$ had been obtained, the material would have been called pseudoplastic, while angles of greater than $45°$ indicate dilatancy. The tangent of the angle is called the pseudoplastic index. Actually, this number represents the exponent of the shear rate in the conventional Power Law equation, which reads:

$$\mathcal{T} = \eta_1 \dot{\gamma}^n$$

Where $\mathcal{T}$ is equal to the shear stress in dynes/cm^{-2}, η_1 is the viscosity at one reciprocal second, $\dot{\gamma}$ is the rate of shear in reciprocal seconds, and n is the Power Law index.

Complicated behavior of this type represents the main reason why one cannot measure the viscosity using a single-point measurement. Instead, a series of measurements must be made and the data interpreted to evaluate the various rheological parameters. It can easily be seen, using Figure 3, that the so-called characterization of structure using the 2 and the 20 RPM method is inadequate. There are any number of possible systems having the same 2 and 20 RPM rates, but different rheological properties. An estimate of the pseudoplastic index is altered when the system possesses a yield value. Therefore, an accurate evaluation of rheological parameters must include a determination of yield value, pseudoplastic index, and the viscosity at a given shear rate - the most convenient shear rate being one reciprocal second. With the cylindrical spindles, the rate of shear is given by the following equation:

$$\dot{\gamma} = \frac{n}{(.2095)\ (RPM)}$$

Where again n is the exponent of the Power Law.

If n is 1, as is the case of the Bingham or Newtonian materials, the RPM at which one reciprocal second occurs is 4.75; but, if n is equal to 0.839, as in the case of a line forming a $40°$ angle, the corresponding RPM becomes 4.0. From the graph of the data, the scale reading at 4 RPM is used to calculate the viscosity by multiplying it by the factor used for the yield value. This viscosity, together with the pseudoplastic index and yield value, will characterize the flow properties of a system.

GELATION TEST METHODS

A great variety of equipment has been used to characterize the plastisol gelation properties. This equipment has varied from a temperature gradient bar to various kinds of viscosimeters. The Brabender plastograph and even an inclined plane viscosimeter have been used. Occasionally, methods based upon the reflection of the plastisol film as a function of temperature have been employed. Some of these methods simply determine a gelation temperature. While the gelation temperature may be of use for rating various resins, it is of little help to the process engineer. Other methods have concerned themselves with the time to reach gelation and have been presented as a gel time. This also is of only limited value for engineering calculations. Our proposed method of testing this property involves a study of the rate of change of viscosity of the plastisol with respect to time at a constant temperature. To achieve this, a Brookfield viscosimeter is used, and for this test is usually equipped with a No. 7 RVS spindle, which is a simple cylindrical spindle having a diameter of approximately 1/8". The plastisol is contained in a 2.5 cm tube which is immersed in an oil bath at the desired temperature. More recently, the oil bath has been replaced by a constant temperature block. The Brookfield viscosimeter is placed over the test tube with the spindle immersed to the proper level in the plastisol, and scale readings are obtained periodically.

This type of measurement gives the viscosity as a function of time at a constant temperature. As such, the information is more helpful to a process engineer studying such things as slush molding, or rotational molding, because now it is possible to predict the flow properties during processing. Generally speaking, these curves show an initial drop in viscosity as the plasticizer becomes warmer. Finally, the curve reaches its minimum and the viscosity of the system continually increases. For systems that gel in a reasonable period of time, the log of the viscosity versus the time gives an approximately linear plot after an initial transition period has passed. Under these conditions, the rate of viscosity can actually be expressed either as a per cent increase per unit time, or the time required for the viscosity to increase by an arbitrary factor "m". As the temperature is reduced or the plasticizer is increased, the increase in viscosity becomes slower and finally departs from its linear relationship, and in some cases of high plasticizer content, flattens off to a constant value.

In order to properly interpret this data, one must have some idea of the mechanisms involved in gelation. Initially, resin is dispersed in the plasticizer. The presence of the solid phase increases the viscosity of the plasticizer to its initial viscosity which may be several hundredfold greater than that of the pure plasticizer. Many attempts have been made to achieve closed mathematical expressions which will relate the viscosity of the suspension to the volume fraction of the resin and the plasticizer. Some of the earlier attempts to do this, such as the work of Mooney, have resulted in a master curve relating the relative viscosity to the volume fraction of solid contained in the suspension.[1] Unfortunately, this system does not take account of the effect of particle size on the resultant viscosity and can be considered only a first approximation. Furthermore, the relationship becomes less valuable as the system becomes more crowded. As the plastisol is heated, or for that matter, as it is stored at any temperature, there is a diffusion of plasticizer into the resin particle. This diffusion increases the particle size of the resin and decreases the relative free-plasticizer volume remaining. As a result of this, the system increases in viscosity. This diffusion causes an increase in the resin particle size until the resin particles become so large that they touch each other and the system is immobilized. This is frequently referred to as the gel point. The critical resin volume required for gelation should remain relatively constant for a given resin since in a given resin, there is no change in the geometry.

There are cases, however, where a large amount of plasticizer is used and the resin may swell to a maximum volume and reach an equilibrium. When this happens, the system does not gel but achieves a certain viscosity and remains at this viscosity. The maximum amount of swelling that can take place would be a function of the resin's molecular weight and the diffusion constant for the particular plasticizer used. This diffusion constant, of course, is highly temperature dependent so that different results may be expected at different temperatures.

One of the best expositions of this phenomena has been described in a paper by K. L. Hoy,[2] who used the reflection from a film as the criterion for the phenomena that is taking place. He reasoned that when the resin phase became so great that there was not enough plasticizer to keep it submerged, the peak of the resin would protrude through the film and that the reflection of this film would be markedly decreased. He also indicated by the application of Frick's Law of Diffusion to a spherical particle that the change in volume, related to plasticizer concentrations and expressed as a fraction of the total change possible when put into logarithmic form, would be linearly related to the time. The slope of such a semilog plot would be related to the diffusion constant multiplied by a numerical factor and a factor dependent upon the particle size. For a given resin, these two factors would not change so that a linear relationship will exist between the log of the amount of swelling divided by the total amount of swelling possible versus time will result in an estimate of the diffusion constant - which, of course, would be highly temperature dependent. By defining a critical concentration as that concentration which, when exceeded, produces a system that will not gel but rather goes to a high and constant viscosity, we establish a gelation parameter. If the plasticizer concentration is less than this critical value, gelation is assured.

We have attempted to blend the ideas in Mr. Hoy's paper with the basic concept of a functional relationship (a master curve) relating relative viscosity to the volume concentration of resin in the plastisol system. Such curves were presented previously by Mooney,[1] et al. In this way, it was hoped that the gelation data could be interpreted in a more theoretical way. A number of systems have been studied based upon different plasticizers. It would be difficult to discuss all of these systems in detail. We, therefore, will concentrate on probably the most common plasticizer - namely, di-2-ethylhexyl phthalate, herein referred to as DOP.

Our first problem was to determine whether or not the system gelled. In order to do this, we have regarded gelation as being infinite viscosity. Of course, we know that the system is not at an infinite viscosity at gelation, because even after fusion, it still has a finite viscosity. This concept is a mathematical convenience and will enable us to extrapolate our curves and find a gel time. Using the normal method of presenting data - namely, plotting the log of the viscosity against time for a given composition of plastisol - one usually can predict the system will gel when the lines are very steep; and, at the other extreme when these lines curve over and flatten, no gelation is indicated (Figure 4). The intermediate values are indeed difficult to assess.

An improved method that we have used to determine the gel time was to plot the time in minutes against the reciprocal of the scale reading. Figure 5 indicates a series of curves showing gelation of di-octyl phthalate at 160°F. for various parts of plasticizer. From this curve, it is clear that 60, 70 and 80 parts per hundred of resin intercept the axis in a finite value, and this value can be considered the gel time. However, when one reaches the 90 parts per hundred, it is apparent that the curvature of the line is such that it will become asymptotic to the infinity axis but not cross. Therefore, the 90 parts per hundred resin does not represent a formulation that will gel, but rather will approach some

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constant viscosity. Similar curves are obtained at other temperatures; however, as the temperature is raised, the lines representing the relationship between the time in minutes and the viscosity as scale readings become flatter for those formulations that will gel. Again, an asymptotic value is approached on those systems that will not gel. This method, therefore, is capable of giving us the gel time from the data obtained.

In the case of those systems that do not gel, it would be enlightening to know what the limiting viscosity might be. Therefore, a reciprocal plot was again used. This time the scale reading was plotted against the reciprocal of the time in minutes. Figure 6 shows such a plot. While the plot of scale reading versus reciprocal time appears to produce a reasonably good line, there is some curvature found in the latter portions of this plot. A straight line extrapolation indicates that the limiting viscosity would be 117 scale units. However, if the curvature in the latter portion of this graph is taken into account, it would appear that gelation might occur somewhere around 125 minutes. Now, extrapolation becomes a little sharper if instead of plotting the scale reading, one plots the logarithm of the scale reading. In this case, the curve becomes linear after a period of time, and extrapolation is simpler. By this technique, we also find that the limiting viscosity would correspond to 125 scale units. Incidentally, the use of the logarithmic function also makes extrapolation of gel time a little simpler because it tends to flatten out the curves of systems that gel. Thus, by use of reciprocal paper, we are able to obtain the time to gelation as well as the constant viscosity that the systems reach at an infinite time. These values for DOP based upon various plasticizer levels and various temperatures, as well as the volume fraction of resins present in each system, are displayed in Table I. Notice that although several systems were tested with 60 parts of plasticizer per 100 parts of resin, the volume fraction is different at each temperature because the plasticizer and the resin do not have similar coefficients of expansion. In this case, the 90 phr system at 180° gelled, but the 95 phr system did not. Therefore, the critical concentration for gelation is somewhere between .426 and .413 volume fraction of resin. We have estimated this value to be .410. Similarly, for other temperatures - namely, 160 and 170°F - we have also arrived at a critical concentration for gelation. This value is referred to as C_e.

Figure 7 displays the gel data for the DOP system in a more or less conventional way showing the time in minutes required for gelation as a function of temperature and as a function of parts of DOP present. Although this is a convenient way of expressing the data in the table, it is of little theoretical significance. If we pursue further the arguments presented by Mr. Hoy, we find that a plot of the concentration of the resin minus the C_e value when expressed as a logarithm is linearly related to the time. Using the estimated values for C_e, we have plotted log of $C-C_e$ versus gel time in minutes (Figure 8), and indeed get very good straight lines. Actually, if the estimate for C_e is off by an appreciable factor, these lines will not be straight but rather will show discernible curvature. Thus, by an entirely different approach, we have been able to confirm some of Mr. Hoy's hypotheses. In pursuing this a little further, we must note that if our gel time had been wrong by some constant amount, it would make little difference in these curves since it would merely shift the curve over to the right or to the left. This is important since one of the most difficult and uncertain measurements in this system is the exact time for gelation. The reason for this is we do not know when time began. Let us consider what happens in the first few minutes: The material in the test tube becomes warmed, the viscosity decreases, and at some point it starts to build up in viscosity. Our question is: What is the zero time? This would normally be considered the time at which the material reached the temperature of the bath and could easily be determined. However, during the period of warming up, a certain amount of diffusion was already taking place so that the

true zero time would not be that at which temperature is achieved, but rather some value different from this time. If we knew what this zero time was, we could read the value of log $(C-C_e)$ from the graph at zero time; this would correspond to the value of C at the volume required for gelation. That is to say, it would be the volume that the resin must occupy in order for the particles to become in contact with one another. We would indeed like to know this value; but up to the present time, we have not found a simple way of determining the zero time value.

If we consider the slopes of the lines on this log $C-C_e$ plot and realize that they arerelated to the diffusion coefficient, we can plot the slope of the line in an Arrhenius Law plot. When this is done as in Figure 9, we see that an excellent linear relationship is obtained. Because the slope of this line is related to the diffusion constant multiplied by a series of factors, we have referred to the slope as a relative diffusion constant. We are presently working on the design of a viscosimeter that will raise the sample to its constant temperature in a very short period of time and thus reduce this error in determining the zero time. However, we have no data available at this time.

In the cases where gelation is not obtained, we have plotted the logarithm of a maximum viscosity (as a scale reading) versus the temperature, and indeed find good straight lines for each particular plasticizer concentration. Figure 10 shows one such graph. In this case, the plasticizer happens to be normal octyl decyl phthalate (NODP). A plot can also be made showing the logarithm of the maximum viscosity versus the plasticizer content in phr, where we obtain different lines for each temperature; and again we seem to have a linear relationship. In all probability, if the reciprocal of the absolute temperature had been used instead of the temperature for the plot in Figure 10, similarly good lines would have been obtained because the range of temperature which we are investigating is relatively limited.

To summarize, the purpose of our presentation was primarily to indicate simple methods of evaluating flow and gelation. As technology advances, more sophisticated methods of evaluating rheological properties are required. The techniques disclosed in this paper permit a fairly complete characterization of flow properties with relatively simple instruments, found in most plastics laboratories. If the yield value, thixotropic coefficients, plastics viscosity, and Power Law index are determined, the low shear rate properties of the system are fairly well characterized. No doubt future requirements will become even more refined. But up to the present, people have not been availing themselves of the full potential of the instruments they now have.

The characterization of gel properties is still very confused, but the systems described here enable one to determine if a system gels at a given temperature and will indicate the critical plasticizer level beyond which gelation is not achieved. Furthermore, the evaluation will give measures of the actual viscosity existing up to gelation. Such information is useful in understanding the flow characteristics in this important pregelation period.

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APPENDIX

BROOKFIELD SCALE FACTOR TABLE
(Cylindrical Spindles)

Spindle	Yield		Viscosity	
	f_t	f_a	F_t	F_a
LV-1	1.98	1.72	9.45	8.21
LV-2	8.07	7.11	38.5	33.9
LV-3	30.8	27.4	147.0	130.0
RV-7	90.0	83.8	430.0	400.0
LV-4	146.0	134.0	698.0	638.0
LV-5	300.0	260.0	143.0	1286.0

The factors given above are designed to convert scale readings using the LV spindles to either yield value (dynes/cm^{-2}) or viscosity (poise). The former is obtained by multiplying the scale intercept by the f factors. This also converts the scale reading to a stress value $\mathcal{T}$ in dynes/cm^{-2} for any reading. The viscosity factors F are used to convert the scale reading divided by the rpm to viscosity in poise. This is true for Newtonian and Bingham bodies; but for power law fluids, an addition factor n, the exponent of the power law, must also be used as a multiplier. This corrects for the change in rate of shear $\dot{\gamma}$, which has been shown to be $(2\Omega/n)$.

Two sets of factors, indicated by a subscript "t" or "a", are shown. The first is based upon a direct calculation based on the actual diameter and the length of the spindle; and as previously mentioned, assumes the end effect is insignificant. This will only be true if the cylinders are very long, which they are not, or if the wall of the vessel is very close to the cylinder. Such conditions exist if the spindle is used in a small test tube or close-fitting metal tube. The second values, indicated by a subscript "a", are based on using a longer fictitious length. The increase in length compensates for the end effect. These values have been determined by the Brookfield people based upon empirical corrections worked out with Newtonian fluids. There is a hazard in applying these to power law fluids, but they certainly can be used in large vessels as a first approximation. The error is most significant when absolute values are required and when n deviates widely from the value unity.

TABLE I

PLASTICIZER-DOP

Parts per Hundred of Resin, PHR	180°F			170°F			160°F		
	Volume Fraction of Resin φ	Gel Time, min.	Max. Visc. in Scale Reading for Non-Gel Systems	Volume Fraction of Resin φ	Gel Time, min.	Max. Scale Reading for Non-Gel Systems	Volume Fraction of Resin φ	Gel Time, min.	Max. Scale Reading for Non-Gel Systems
60	0.528	11.6	--	0.528	14.7	--	0.530	19.1	--
70	0.489	12.7	--	0.490	16.7	--	0.491	22.2	--
80	0.456	13.8	--	0.457	17.8	--	0.458	27.4	--
90	0.426	16.2	--	0.428	21.6	--	0.430	--	352
95	0.413	--	360	0.415	--	257	0.416	--	--
100	0.401	--	165	0.402	--	125	0.403	--	--

FIGURE I

BROOKFIELD VISCOSITY DATA

PLASTISOL COMPOSITION:
BLACAR 1715 - 100 PARTS
D.O.P.   - 60 PARTS

CURVE NO. 3

LINE NO. 2

LINE NO. 1

SCALE READINGS

RPM - REVOLUTIONS PER MINUTE

FIGURE 2

LOG-LOG PLOT
OF BROOKFIELD VISCOSITY DATA

LOG OF SCALE READING

LOG OF RPM

FIGURE 3

VISCOSITY AND YIELD VALUE
OF VARIOUS SYSTEMS THAT WILL
HAVE AN APPARENT BROOKFIELD
VISCOSITY OF 60 POISE AT 2 RPM
AND 25 POISE AT 20 RPM

η

Y

n - POWER LAW INDEX

FIGURE 5

DI-OCTYL PHTHALATE
GEL CURVE AT 160°F

90 PHR
80 PHR
70 PHR
60 PHR

TIME IN MINUTES

SCALE READING

FIGURE 6

DI-OCTYL PHTHALATE

GEL CURVES AT 170°F USING 100 PHR

LINEAR PLOT
LOG PLOT

LOG OF SCALE READINGS

SCALE READING

TIME IN MINUTES

FIGURE 4

PLASTISOL GEL CURVES

AT 160°F

60 PHR
70 PHR
80 PHR
90 PHR
95 PHR
100 PHR

SCALE READING

ELAPSED TIME IN MINUTES

FIGURE 10

GEL CURVE MAXIMUM

DODP/BLACAR 1716

MAXIMUM VISCOSITY (SCALE READING)

TEMPERATURE, °F

80 PHR

90 PHR

100 PHR

FIGURE 9

ARRHENIUS LAW PLOT

RELATIVE DIFFUSION RATE CALC. FROM GEL CURVES

DOP AND BLACAR 1716

SLOPE RELATED TO DIFFUSION CONSTANT

RECIPROCAL ABSOLUTE TEMP. $1/K \times 10^{-5}$

160°F   170°F   180°F

FIGURE 7

GEL TIME VS. TEMPERATURE AND PLASTICIZER CONTENT

DOP AND BLACAR 1716

TIME TO GEL (UNCORRECTED) IN MINUTES

TEMPERATURE

PHR OF DOP

160°F   170°F   180°F

90 PHR   80 PHR   70 PHR   60 PHR

FIGURE 8

PLOT OF LOG $(C-C_e)$ VS. GEL TIME

BLACAR 1716 AND DOP

60 to 90 PHR

LOG $(C-C_e)$

GEL TIME IN MINUTES (UNCORRECTED)

CALCULATION OF SLOPE:		
	TIME/DECADE	SLOPE
180°F	5.14	-0.448
170°F	7.58	-0.304
160°F	12.38	-0.186

180°F   170°F   160°F

VINYL FUSION INDICATOR

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This paper relates to the use of fusion or curing indicators for determining the completion or stage of fusion of a pigmented vinyl material such as vinyl plastisols, organosols or other compounded vinyls. More particularly, the paper will describes a method for determining such fusion or curing by fluorescence in the presence of invisible radiation.

In the industrial processing of pigmented vinyl dispersion, such as vinyl plastisols and organosols, heating conditions are often difficult to precisely control. Under an assumed set of conditions, the degree of fusion of a finished object may vary significantly. For example, in the rotational casting process for making sypherical circular objects, a multiplicity of aluminum cavities are mounted on spindles. When filled with plastisols, the closed cavities are rotated in a heated forced air oven. The circulating air stream does not always heat each cavity uniformly thus resulting in plastisol objects which have not been equally heat treated. Further, changes in the velocity of air and rise and fall in temperature of oven heat are unpredictable and may not be noticed by the operator.

Because of these variations, the physical properties of the finished objects will vary. Such variance in physical properties is often sufficiently wide enough that some of the finished objects will fall below the acceptable minimum standards the producer. The number of "rejects", of sub-minimal standards, which may thereby be produced may be large and the economic loss considerable. Thus, it is desirable to provide some means for indicating the extent to which plastisol has been fused, at a time when the equipment can be adjusted and the cure can be conveniently continued or discontinued for the elimination of such "rejects".

Former responsive cure indicators such as the thermochromatic cure indicators have been used in cure processes to indicate the attainment of a proper curing temperature. However, such indicators which show merely the attainment of the proper cure temperature need not be indicative of a proper cure or state of fusion, especially when the cure must be carried out at the temperature for a period of time. Further, the use of the thermochromatic curing indicators involves the coordination of the indicator and its color change temperature with a curing temperature of a given plastisol, a coordination which may or may not be possible in a given system. It is, therefore, desirable to provide more widely useable curing indicators which directly indicate the proper cure rather than some temperature at which the cure is possible.

Other cure indicators have been proposed which give a visible color change on

proper cure. However, use of such indicators may result in commercially undesirable and unacceptable coloration of the finished article. It is a general object of this paper to show a new and useful method of determining the fused status of a vinyl compound.

This paper will show a new and useful method which may be used to determine the degree or completion of fusion of a plastisol by changes in the fluorescence of an indicator in the plastisol when viewed under invisible radiation.

In one aspect of this method of fusion indication, it is an object to provide such a method in which the product formed by fusing the plastisol is not appreciably affected in appearance under normal visible light conditions by the presence of the indicator.

The determination of cure or fusion of a fusable vinyl dispersion may be conducted by adding or mixing a fluorescent material with the liquid dispersion or compound, subjecting the dispersion to curing conditions and comparing the color change of the fluorescent material under invisible radiation as a determination that the dispersion is fused or cured.

First, to specifically exemplify this method of fusion indication, a plastisol of the following composition was compounded:

Ingredients	Parts by Weight
Polyvinyl chloride	100
Dioctyl phthalate	70
Calcium carbonate	20
Barium Cadmium stabilizer	2
Antimony oxide	2

Plastisols such as the one above have normal oven curing temperatures in the 250 to 500° F. range. To exemplify the curing indication with this plastisol in invisible light, three portions of the above plastisol were taken and 0.5% of a fluorescent pigment or dye was incorporated into each portion prior to curing. The fluorescent materials, which were mixed into the plastisol, for each of the three runs are as follows:

Run 1	Rhodamine 6GDN
Run 2	Auramine
Run 3	Thioflavin

In each run, the plastisol containing the fluorescent material was heated to a curing temperature of about 350°F. and the cure was studied intermittently under ultraviolet light and an appreciable or distinct color change was noticed in the plastisol. When the cure was proper and was discontinued the intensity of the color was noted. These objects were marked as standards. Thereafter, other experiments using the same plastisols were conducted and curing was continued until the color change matched the standards. At that time, the cure was proper. Where cure was discontinued before the proper color was reached, the plastisols were not properly cured. Further, there was no appreciable change in visible color.

The method of compounding an indicator compound has been generally described and specifically exemplified above. The fluorescent material is included in the dispersion in a minor amount, preferably from about 0.0001 to 2% by weight, although much smaller or larger amounts can be used. With fluorescent dyes, the amount added will generally be at the lower end of the range, while with pigments

it generally will be at the upper end of the range. Mixtures may fall within or without the range.

The amount of fluorescent material will depend, of course, to some extent on the intensity and compatibility of the fluorescent material in the plastisol. However, generally, the fluorescent material may be used in either small or large amounts.

Upon preparation of the mix of fluorescent material and vinyl dispersion for use in producing any desired object, a standard should first be prepared. To do this, an amount of the prepared dispersion is cured for a proper time and at the proper temperature to obtain a proper cure or fusion. This may be confirmed by tensile strength tests and the like. The properly cured object is then viewed under invisible or ultraviolet light and the color intensity is noted. Thereafter, all objects produced using the specific formulation are compared under ultraviolet light with the standard and if the color is the same, the object will be found to be properly cured.

In the alternative, it may be desirable to prepare more than one standard object showing various states of cure and even over-cure so that on comparison of any other objects their state of cure may be readily determined. If the cure is conducted in the presence of substantial amounts of invisible radiation, it may be desirable to take into general account any catalytic or excitation effects that such radiation may have on the cure or on the cured product. This is particularly important where significant doses of ionizing radiation are used or where a radiation activated catalyst is used, e.g., a catalyst activated by ultraviolet light or gamma rays. However, by correct observation of the cure in accordance herewith, the cure can be followed and completion determined.

As indicated above, the cure conditions for a given plastisol are already well known to producers of vinyl products. For the polyvinyl chloride plastisol as specifically exemplified above, we may use, for example, 350° to $750^{\circ}F$. for a period of, for example, 30 seconds to 15 minutes. Cure times and temperatures may be adjusted as desired.

It appears that by using fluorescent material in accordance herewith, the intensity of emitted color of a fused plastisol can be made a function of the heat history, including time and temperature of fusion, of the fused dispersion. This apparently holds true for fluorescent materials and curable vinyl compounds generally, although the colors and color changes may vary widely with different fluorescent materials and/or dispersion. Thus, with a given formulation, the intensity of emitted fluorescent color can be heightened with increases of either time or temperature of fusion or with increases in both.

The formulation can also be designed so that, conversely, the intensity of the emitted color will decrease with increase of time or temperature or both. In like manner, the color or shade will depend on the heat history to which the fused plastisol has been subjected. Additionally, the color or shade of the emitted fluorescence of a fused plastisol will depend, as one factor, on the nature and amount of fluorescent substance and the contents of the base plastisol. Thus, for example, a fluorescent material which shows a definite and readily noticeable color change in one dispersion system may provide only a limited and almost undetectable color change in another system. However, those skilled in formulating vinyls will understand this and will be able to, by experimentation, choose the proper fluorescent material for an intense and noticeable color change on fusion.

When the fused plastisol is observed under ultraviolet light, the color change may be detected by the human eye, color recording instruments, color sensitive instruments, or the like, as the determination of the proper cure. Color change is apparently soundly based and dependent on the history of the dispersion leading to proper cure and hereby can be taken as a correct indication of proper cure.

Intensity is, thus, made a function of heat history but will also depend on the amount of fluorescent material used. As seen above, color or shade of the fluorescence also may be important in the detection of proper cure and may vary somewhat with the particular plastisol used. Upon curing, the fluorescent property changes.

The addition of fluorescent material to the vinyl dispersion with subsequent fusion and exposure to ultraviolet light results in an emitted fluorescence which is a blend of the background color of the dispersion and the fluorescence of the fluorescent material. By associating the degree of fusion with a particular shade and/or intensity of fluorescence of the fused dispersion fluorescent material mixture, there is established a "degree of fusion" or fusion indication.

A set of color standards may readily be prepared for a given plastisol or variety of plastisols, if desired. Such standards can be prepared by imitation of the color for a desired degree of cure or as a set of standards for various phases of cure. More usually, the standard desired is the standard for complete cure, which standard may be a sample of properly cured dispersion of the same composition and including the same fluorescent material in the same amount as the dispersion to be monitored.

As indicated above, detection and comparison with a sample may be made by the human eye or by color responsive instruments, such as a pair of photo-electric cells in a Wheastone bridge arrangement as known to the art for comparing colors.

This appears to be a method which can be used to monitor production of cured dispersion whereby products from a curing zone may be monitored for proper cure and the curing process conditions can be readjusted in accordance with the findings as to proper cure, either manually or by automatic control. The degree of cure may also be monitored or detected if desired and the method is further adaptable for use to determine the cure end point by following or monitoring the cure process continuously or intermittently in the presence of the invisible radiation.

Although a particular plastisol (or dispersion) of the polyvinyl chloride type has been specifically exemplified and used above, other fusible polyvinyl chloride dispersions are, of course, usable. Such other dispersions would be produced by variations in the plasticizer, stabilizer, pigment and/or fillers. For example, plasticizers such as diisodecyl phthalate, aromatic hydrocarbons, tricresyl phosphate, dioctyl azelate and others, are usable. In place of barium cadmium stabilizer, lead, tin, zinc, epoxy and epoxy materials and the like may be used. The amounts of these materials and the like amounts of the polyvinyl chloride may be varied widely.

The fluorescent materials commercially available may be used or suitable materials may be produced for use in accordance with known procedures. The fluorescent material may be a dye or a pigment or mixture thereof and may have visible color characteristics in visible light where it is desired to incorporate such visible characteristics into the cured product. Preferably, however, the fluorescent material is invisible, i.e., non-appreciable, or of a light normally undetectable shade or color in the concentration used under visible light so as not to

appreciably affect the appearance of the cured dispersion in visible light. The material fluoresces under invisible radiation, e.g., when activated by radiation of proper wave length.

The material may be organic or inorganic. The usable fluorescent materials are those which (exist in non-gaseous, e.g.,) are solids or liquids. Preferably, the fluorescent material is compatible with the dispersion in the amounts and under the conditions used and is not totally reactive with the dispersion so as to completely destroy the fluorescent property prior to completion of the cure.

The many fluorescent materials available for use include the ketoimine dyes such as Auramine; the xanthese dyes such as Rhodamine B and Rhodamine 6GDN; diphenyldihydroimidazolones, diaryl and triaryl pyrazolines, aminocoumarins, bis-benzimidazoyl ethylenes, oxacyanines, oxadiazoles such as styryl-oxadiazoles, pyrazolines such as styryl-phenyl-pyrazolines or Thioflavin.

Such organic fluorescent compounds as benzoic acid, beta-naphthol, fluorene, phenanthrene and acenaphthene, may also be usable among many other fluorescent organic compounds. Examples of fluorescent inorganic compounds are strontium, zinc, calcium and/or cadmium sulfide pigments, e.g., zinc-cadmium sulfide mixed fluorescent pigments.

The fluorescent materials are fluorescent in invisible radiation and the radiation of proper wave lengths should be used with the particular fluorescent material selected or the fluorescent material selected may be selected on the basis of the invisible radiation available. Although the method has exemplified with respect to ultraviolet light and ultraviolet light is a preferred source of invisible radiation, other forms of invisible radiation, such as X-rays, infrared radiation and gamma radiation may be used. The radiation need only be of a wave length and intensity sufficient to cause detectable fluorescence in the fluorescent material outside the visible light range.

RHEOLOGICAL REQUIREMENTS OF VINYL DISPERSION

COMPOUNDS FOR FABRIC COATING

PART II*

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The coating of cloth with vinyl plastisols has been and will continue to be an important application of these liquid plastics systems. Vinyl coated cloth of both the regular and foam laminate variety are used in very large quantity as upholstery fabrics for home and auto; for fabrication into ladies' accessories such as hats, handbags, boots, belts; winter jackets for the entire family; truck tarpaulins; and so forth.

Our previous paper[1] on this subject dealt with means by which to prevent plastisol penetration through the cloth when the two lamina are brought together. This is accomplished by developing certain desirable rheological properties in the compound. A heat gelation technique was discussed whereby these rheological properties were properly altered by a controlled exposure to heat prior to lamination. Another technique discussed was the use of compounding additives to bring the room temperature viscosity properties into the desired range.

Laboratory and field experience since have shown that where plastisol viscosity is modified through compounding we are not always able to predict penetration performance from simple room temperature viscosity data for the plastisol compound. This circumstance may be demonstrated in the laboratory by the preparation of a plastisol-cloth laminate.

Here a plastisol compound is doctored onto a suitable substrate, such as a glass plate or release paper. Then a knit-type fabric is laminated to the wet plastisol using the pressure supplied by a wooden roller as shown in Fig. 1. This simulates the actual production technique.

Differences in the penetration performance of three compounds are shown in Figure 2. Compound X exhibits no penetration initially, i.e., while the plastisol is still fluid before its gelation, or after fusion. Compound Y exhibits no penetration initially but marked penetration is evident when the laminate is removed from the fusion oven. Compound Z shows some penetration initially and more after fusion.

These observations could not be predicted from the room temperature viscosity of these compounds, also noted in Fig. 2, e.g., the highest viscosity compound (Y)

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exhibits considerable, and totally unacceptable strike-through!

The differences in penetration performance from compound to compound before gelation and after fusion suggest important changes in the rheological character of each plastisol are occuring as the plastisol goes from room temperature through its pre-gelation stage up to gelation. All are undoubtedly familiar with the classical viscosity reducing affect of applied heat as the plastisol passes through pre-gelation on its way up to gelation and fusion temperatures. This is the natural result of the thinning out of the plasticizers as the temperature rises but prior to gelation as mentioned above.

Utilizing a gelation plate apparatus (Figure 3) it is readily seen that compound Y(@ 475,000 cps) thins out during its passage through pregelation resulting in the plastisol penetrating through the cloth, even though compound Y was considerably more viscous than X (@ 240,000 cps) at room temperature which as seen in Figure 2 resists penetration completely.

A more quantitative understanding of the viscosity changes occuring during pre-gelation is obtained using the apparatus shown in Figure 4 and further described.[2,3] Here a Brookfield viscometer is mounted over a plastisol compound held in a metal tube which is immersed in an oil bath. The bath is maintained at some elevated temperature designed to bring the compound up to gelation in a reasonably short period of time. Viscosity is continuously recorded as the plastisol heats until it reaches its gel state. Plastisol temperature is obtained by means of a thermocouple probe resting in the sample contained in the tube.

Data on compounds X, Y and Z using this technique are shown in Figure 5. Viscosity versus plastisol temperature is plotted. The poor performance of compound Z can be explained on the basis of its low initial viscosity and the even lower viscosity it attains during pre-gelation. However, these data fail to show why compound Y has performed so poorly. Its curve matches rather closely to compound X, whose performance was very satisfactory.

The plot of viscosity versus temperature as shown in Figure 5 does not describe the time a plastisol is in its reduced viscosity state. A new plot of these data (Figure 6) shows this. Now, although the minimum viscosities for X and Y are similar the length of time compound Y is at its minimum viscosity is many times that of compound X. Hence, the longer dwell of a compound in an intermediate viscosity range is as conducive to fabric penetration as dropping to a lower viscosity.

Having established the important features of the viscosity curve during the pre-gelation period of a plastisol compound with respect to predicting cloth penetration or strike-through performance, a homologous series of compounds were prepared to illustrate the use of this analytic technique in developing a compound without resorting to costly plant trial (and error) methods. For the purposes of illustrating this principle the following base formulation was selected.

PVC resin (MARVINOL[R] 50)	100
Plasticizer (DOP)	55
Epoxy plasticizer (Flexol EPO)	5
Ba, Cd, Zn stabilizer (Mark KCB)	3
Pigmentation (black paste)	3

An evaluation of the compound as is, using the lab technique shown in Figure 1, i.e., applying fabric to a liquid plastisol casting, quickly shows the need for building up its low shear viscosity to prevent fabric penetration. Many materials are available to do this. For this particular study Santocel Z, a high oil absorption material, was used.[4,5]

Laminates prepared from compound with varying levels of Santocel Z are shown in Figure 7. Note that in only two instances penetration control appeared to be satisfactory just after lamination but the degree of fluidity developed in the compound during its pre-gelation warmup is sufficient to allow the plastisol to penetrate the cloth in all but the sample with 3 parts of Santocel Z. Thus only at the 3 phr level was complete penetration control achieved.

Penetration control has been achieved but is the compound capable of high speed coating. Figures 8 and 9 depict the low and high shear viscosity properties of this series of compounds as a result of its modification with Santocel Z.

The rheological requirements of a compound for high shear coating have been described.[6,7,8,9] The high shear viscosity of the compound containing the necessary level of Santocel Z, i.e., 3 phr, is clearly too high. The addition of a naphtha diluent (V, M & P or mineral spirits) will reduce high shear viscosity. Fortunately, diluents reduce high shear viscosity at a faster rate than its viscosity reducing effect at low shear.[6] Consequently, much of the beneficial bodying action of Santocel Z is retained. The addition of 2 phr of diluent coupled with the use of Santocel Z brings the Severs viscosity of this compound into a useful range. This is shown in Figure 9.

A final finesse to the development of this compound would be an attempt to bring down the Santocel Z level. As seen in Figure 10 its reduction below 2.75 phr results in strike-through. The final compound then contains 2.75 phr of bodying agent and 2 phr of diluent. The resultant rheological properties provide both cloth penetration control and high shear coatability.

The use of viscosity modifiers such as high oil absorption pigments and naphtha diluents may prove to be a perfectly workable solution to a coating problem. However, the problems associated with this approach become immediately apparent when the high pound cost and high density of such viscosity building additives are considered along with the additional compounding involved to properly incorporate them into the plastisol. Also, volatile diluents in the coating which must be evaporated during fusion present obvious hazards which can only be disposed of with a properly engineered oven exhaust system. Consequently, the investigation must be continued to find alternate formulations that will develop the desired cloth penetration control.

As pointed out in the first section of this paper, the pre-gel viscosity versus time curve is the only parameter by which we may accurately predict compound performance other than the actual preparation of a laminate. Such an analysis may be useful in providing a quality control device for successive batches of this compound and in the development of new compounds. The pre-gel viscosity curves for several of these compounds are shown in Figure 11.

Penetration properties directly after lamination but prior to pre-gelation thinning out are indicated on each curve at zero time. The final penetration properties after fusion are noted at the minimum viscosity point for each curve since it is this viscosity value that is most relevant to predicting such performance. A comparison of these two sets of observations shows that a drop below

the critical low-shear viscosity at room temperature or any temperature in the pre-gel region results in penetration. In this case, this is estimated at 100,000 cps. This will vary depending principally on the weave of the particular cloth employed.

It will be noted that a compound exhibiting a minimum viscosity of ca. 100,000 cps during pre-gelation is over 200,000 cps at room temperature. This could prove to be troublesome for a number of reasons. A plastisol compound at this viscosity level may be difficult to mix with marginal mixing equipment. It may be difficult to deaerate. It may difficult to pump to the coating head.

These curves suggest that a flat viscosity-gel curve or a more rapid transit through the pre-gel period may allow a compound to operate with a lower room temperature Brookfield viscosity without allowing cloth penetration. This may be accomplished through the use of selected plasticizers and/or resins of the rapid gelation type.

In the first example TCP, a highly solvating plasticizer, was evaluated. Pre-gel curve data are shown in Figure 12 in comparison with some of the curves from Figure 11. This compound with its room temperature viscosity of 136,000 cps is almost half the viscosity required for the formulation used in Figure 11. However, the use of TCP or other solvating plasticizers may not offer a practical solution to this coating problem because of the cost, odor, volatility or inadequate cold temperature properties of such plasticizers. Its use here is principally to illustrate the minimum pre-gelation viscosity concept and how plasticizer selection may bring about a more workable compound.

Another approach to a sharper gelation curve may be through resin selection. The use of solvating plasticizers, notwithstanding any undesirable properties associated with their use, suggests the use of a copolymer dispersion resin. Figure 13 illustrates the use of MARVINOL(R) 56, a vinylchloride-acetate copolymer with a conventional plasticizer system based on DOP. The rapid gelation character of the MARVINOL(R) 56 based compound as shown in Figure 13 again allows operation with a lower room temperature viscosity compound by shortening the period the compound is in its low viscosity state.

Here again, the completely practical approach to a coating problem is hampered by the use of a copolymer resin with the lower physicals, reduced plasticizer migration resistance and other defensive qualities generally associated with copolymer resins.

What is needed for a completely satisfactory solution to this coating problem is a homopolymer resin specifically designed to provide penetration control without the need for viscosity modifiers, special plasticizer selection or the use of copolymers. It is quite possible through astute resin selection to develop a satisfactory compound.

In Figure 14 a unique blend consisting of MARVINOL(R) 50 and MARVINOL(R) X6215S, both homopolymer PVC resins, develops the desired gel curve without resorting to the use of any viscosity building agents. Here again a lower room temperature viscosity has been developed without loss of penetration control.

Gelation temperature[10] as a criteria by which to judge this phenomenon has not been used in this paper. Gelation temperature data for the compounds used in Figure 11 are noted. Although they correlate on a qualitative basis with the viscosity-gel curve data they lack sufficient quantitative definition to be useful.

In this work the viscosity data have been reported on the basis of a single point value. The changing shape of the plastisol compound's flow curve during pregelation may be of interest. Figure 15 is a rheograhm of a compound at room temperature; at its minimum viscosity point; as its viscosity begins to advance; and finally, when it has advanced to a point roughly equivalent to its room temperature value. The major change in the viscosity character of the compound is the marked increase in yield value, as measured by the deflection axis intercept.

As previously noted the cloth used has a profound bearing on the viscosity requirements of the compound for satisfactory penetration control. Figure 16 illustrates this with a photomicrograph of a heavy and a light cloth. Both are coated with the same compound. Note the marked penetration through the open weave cloth.

There are many facets to this work that will warrant further study. Field experience will dictate into which areas such study will be directed. The author wishes to acknowledge the helpful assistance of Mr. W. Keith Swinehart in the accumulation of laboratory data for this report, and to Mr. Ivan Mankowich, Manager of MARVINOL(R) Research & Development, in the preparation of this manuscript.

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Penetration

	Just After Lamination	After Fusion
Compound X 240,000 cps*		
Compound Y 375,000 cps*		
Compound Z 82,000 cps*		

*Brookfield Viscosity

FIGURE 2: Penetration Properties of Plastisol Compounds

FIGURE 4: SPI Viscosity-gelation Apparatus
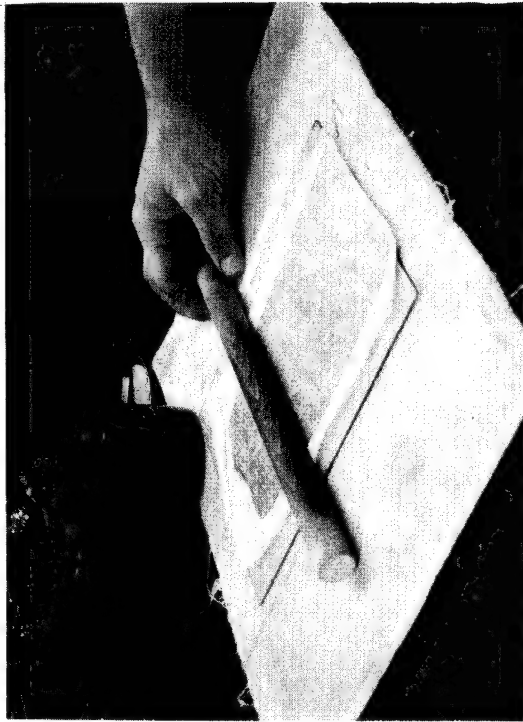
FIGURE 1: Preparation of Plastisol-Cloth Laminate
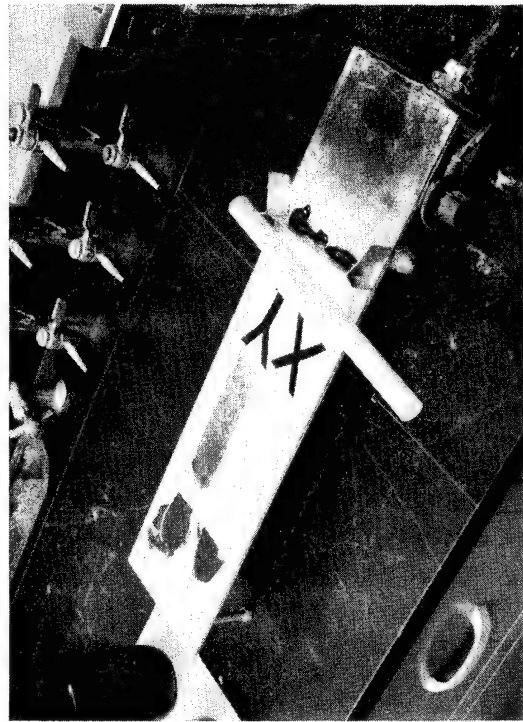
FIGURE 3: Penetration of Compound Y during Pre-gelation
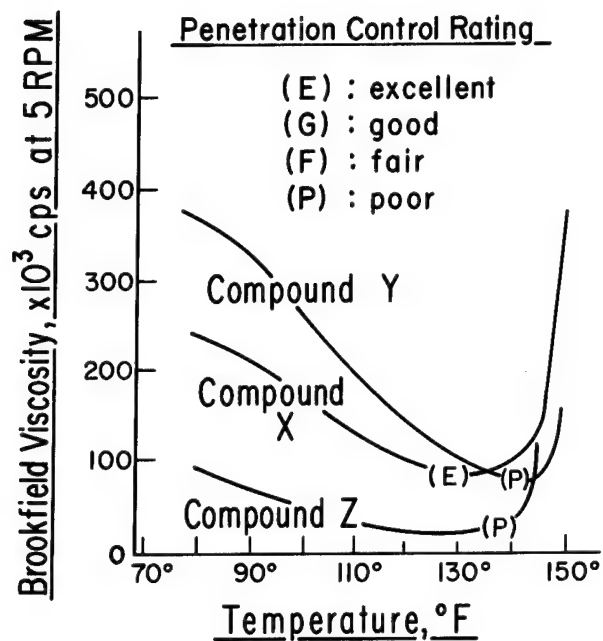
FIGURE 5: Plastisol Viscosity Versus Temperature
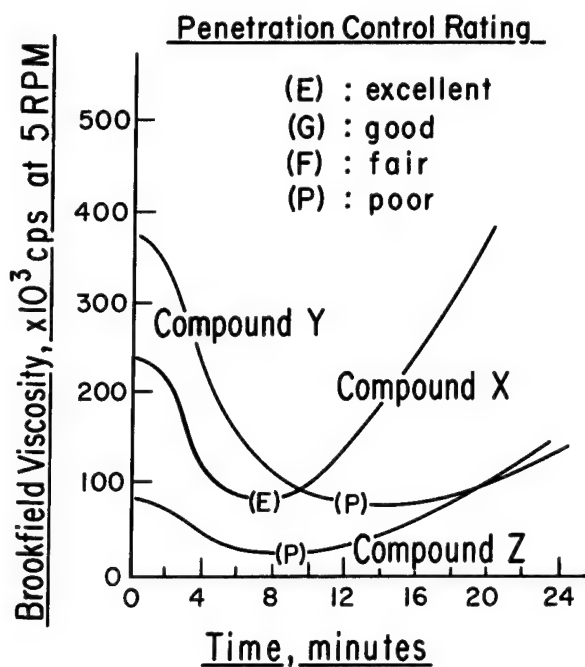
FIGURE 6: Plastisol Viscosity Versus Time

FIGURE 7: Penetration Properties of Compounds Modified with Santocel Z
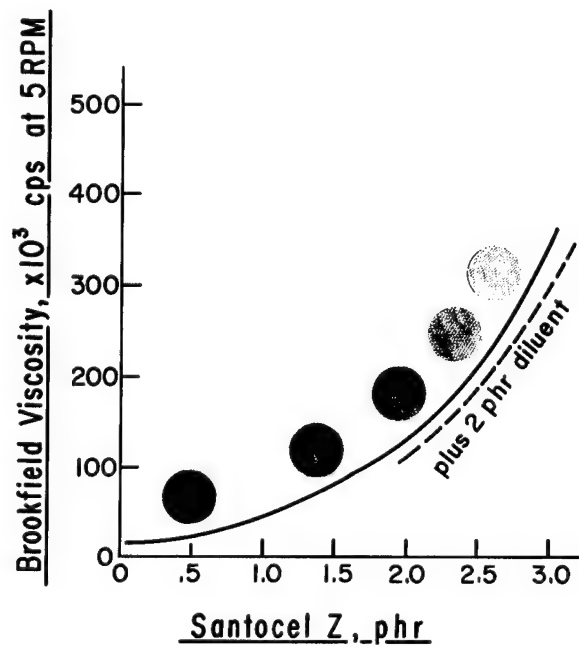
FIGURE 8: Low Shear Viscosity Properties
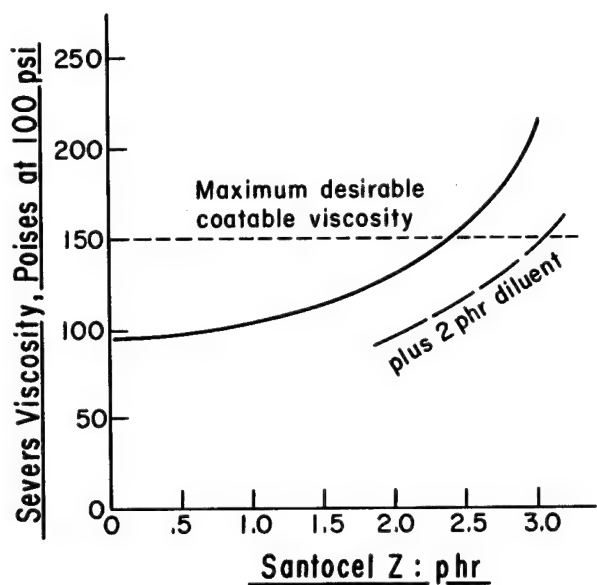
FIGURE 9: High Shear Viscosity Properties
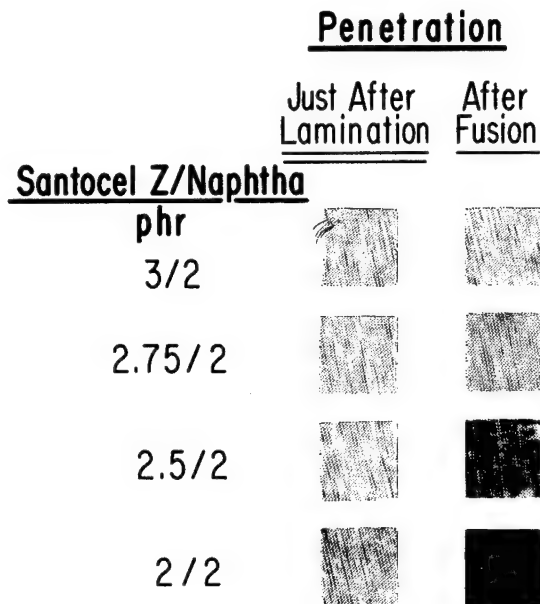
FIGURE 10: Penetration Properties of Compounds Modified with Santocel Z and Naphtha
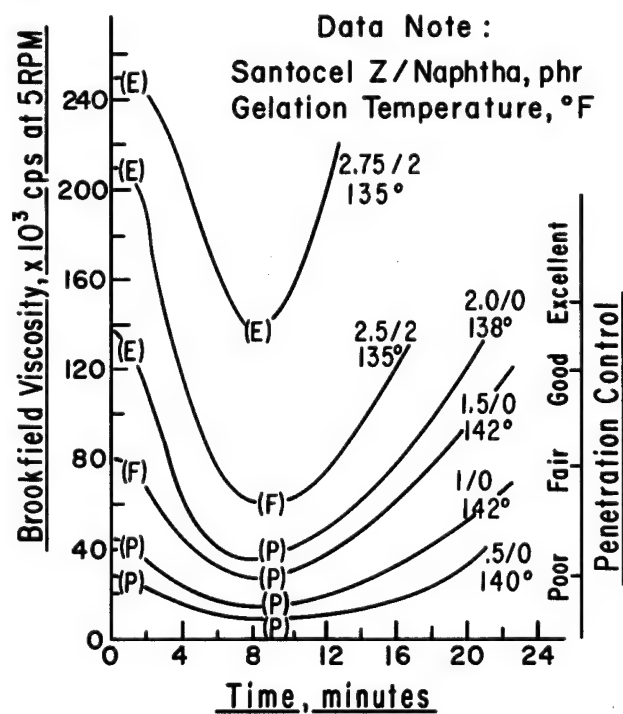
FIGURE 11: Plastisol Viscosity Versus Time
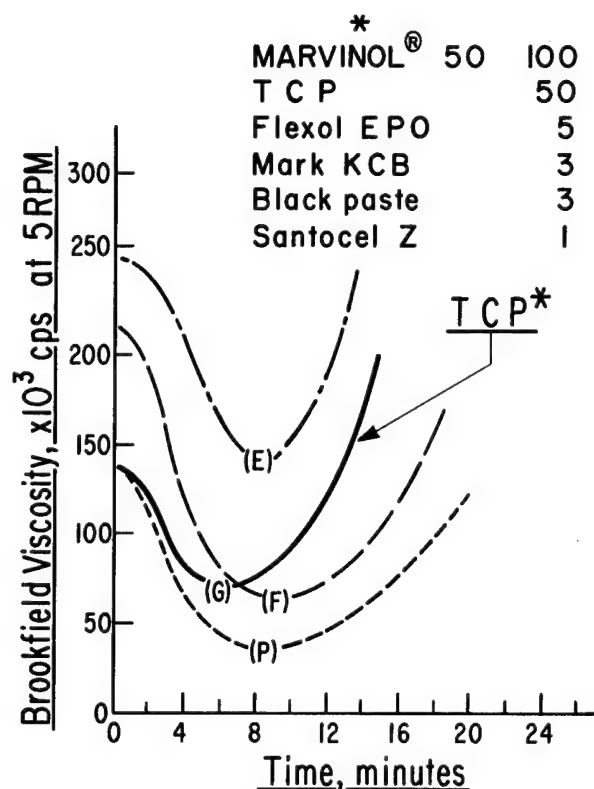
FIGURE 12: Gel Curve for TCP Based Compound
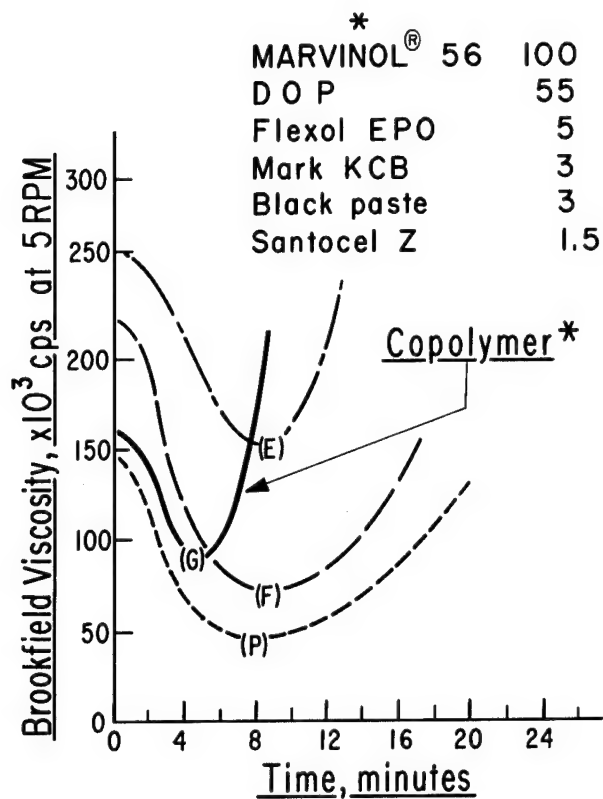
FIGURE 13: Gel Curve for a Copolymer Resin

MARVINOL® 56	100
D O P	55
Flexol EPO	5
Mark KCB	3
Black paste	3
Santocel Z	1.5
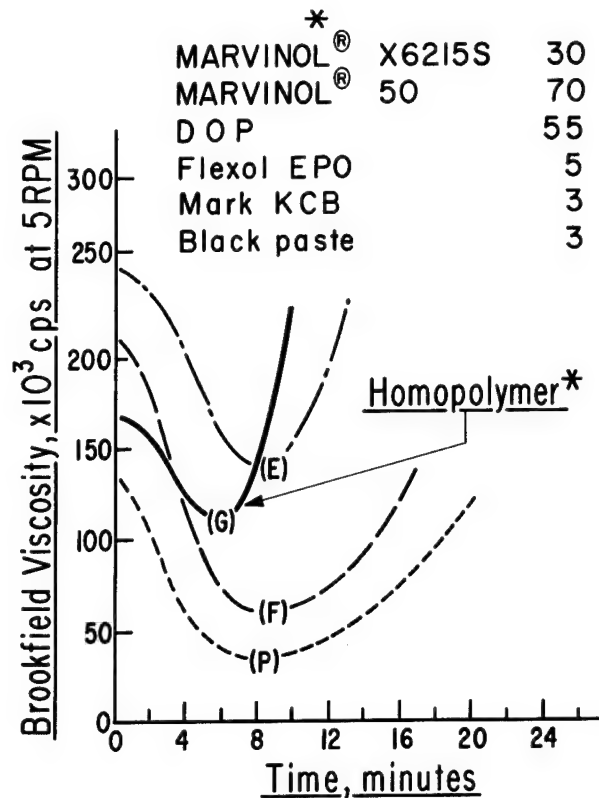
FIGURE 14: Gel Curve for Marvinol X6215S/Marvinol 50 Based Compound

MARVINOL® X6215S	30
MARVINOL® 50	70
D O P	55
Flexol EPO	5
Mark KCB	3
Black paste	3
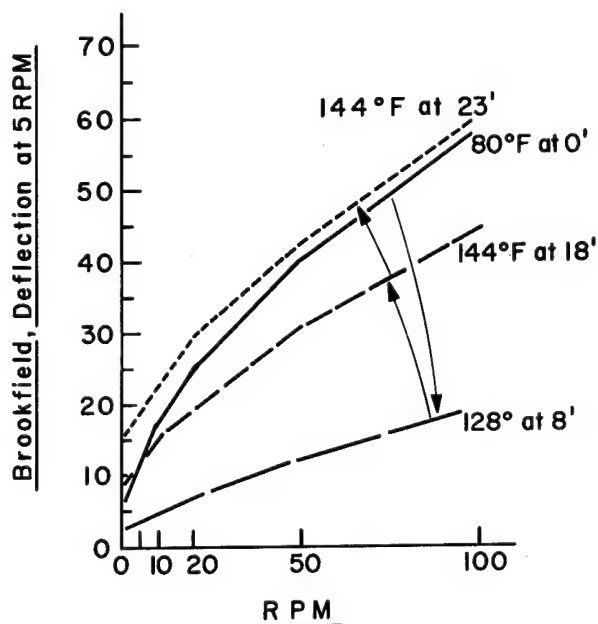
FIGURE 15: Rheograhm During Pre-gelation
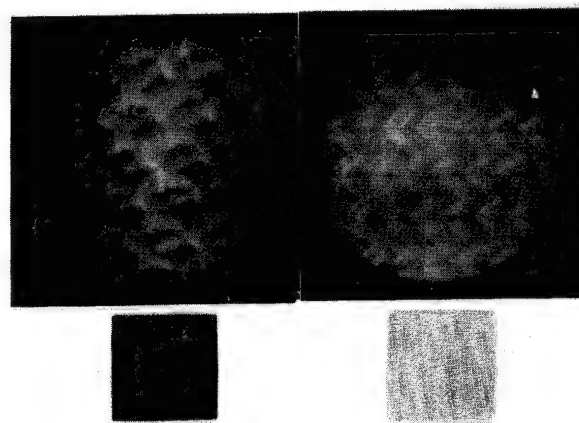
FIGURE 16: Penetration Properties as a Function of Cloth Selection

VINYL CHLORIDE-ACRYLIC POLYMERS AS EXTERIOR COATINGS

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INTRODUCTION

The combination of alkyds with vinyl chloride-acrylic polymers results in ex-
terior latex paints having improved performance over difficult surfaces. The use
of alkyd-latex mixtures is a commercial practice which appears to be of particular
value with vinyl chloride-acrylic latex polymers. The similarity of alkyds to con-
ventional plasticizers for vinyl chloride polymers is believed to be the reason
that mixtures of these two materials are giving superior performance.

The excellent performance of vinyl chloride-vinyl acetate copolymer solution
resins, as binders in paints for a variety of outdoor applications, e.g. main-
tenance paints, marine paints, aluminum siding, demonstrates the utility of vinyl
chloride as a useful basic building block for polymers with exterior durability.

The proven capabilities of this molecule to deliver outdoor performance make
it logical to extend its use to other outdoor applications. The exterior trade
sales field, long dominated by drying oil and alkyd binders, is finding increasing
uses for polymeric binders in the form of latex emulsions. Since a prime requi-
site of all exterior paints if film formation at low temperatures (40-50°F), it is
necessary to copolymerize vinyl chloride with softening monomers to obtain a
polymer suitable for paint. Vinyl acrylic esters are effective softening monomers
for vinyl chloride. They also are noted for their exterior performance. The com-
bination of these monomers has resulted in vinyl chloride-acrylic polymers with
low enough film-forming temperatures for exterior emulsion paints.

The exterior trade sales paint industry is an old industry which, in order to
prosper, has had to formulate paints that would perform satisfactorily when ap-
plied by customers unfamiliar with paint technology. Frequently, the customers
apply paints to substrates and under climatic conditions that make the paint tech-
nologist despair.

The industry has met these marketing conditions by developing specialty
paints which optimize performance on substrate types, i.e. wood paints, masonry
paints, trim paints, self-cleaning paints and primers. Customer education as to
proper usage through can labels and retail merchandise is another feature of this
industry. As the manufacturer's liability is relatively high in relation to the
cost of the product, he finds it necessary to overdesign paints which, hopefully,
will perform adequately on the 5 to 10% of the homes that have serious paint
problems.

An exterior paint is expected to protect and decorate. Technically, this means that a pigment binder must resist climatic conditions and must adhere to pigments and to the substrate. The combination of pigment and binder must be stable in a container for several years over the temperature range encountered during shipping, warehousing and retailing. At any time after manufacture, it must have rheological properties that allow it to be applied readily and to form rapidly a protective, decorative coating with a life of several years.

The paint technologist, therefore, has as a continuing objective the utilization of binders which meet these requirements best at the lowest cost consistent with the expected performance.

Historically, the paint industry has met this challenge by ingenious combinations of materials. The industry now has at its command different binder classes. The drying oil or alkyd class is composed primarily of low-molecular-weight liquids (monomers or very-low-molecular-weight polymers) containing oxidative sites. These materials can, by the use of oxidative catalysts, be transformed rapidly to tack-free polymers by oxygen linkages. Also available are medium-molecular-weight polymers with or without oxidative sites dissolved in, or thinned by, volatile additives. In the past twenty years the development of synthetic latexes has added the high-molecular-weight polymer with or without oxidative sites to the paint chemist's arsenal.

The environment to which an exterior paint is subjected is:

1. Temperature ranges of more than $100^{\circ}F$.
2. Water in the three forms - ice, liquid and vapor.
3. Oxidative atmosphere plus ultra violet radiation.
4. A variety of industrial dirt and fumes.

If the only requirement of a paint film were its ability to withstand the environment, the capability of the high-molecular-weight, saturated polymers in the above conditions would rapidly result in their exclusive use. There are, however, other important considerations. This is a consumer industry and one characteristic of this consumer is that he wants to do the least possible physical work. With this as a guiding principle, the consumer has made known his wants and by his buying power has enforced his dictates of:

1. Easy, rapid application - There are many facets to this demand.

      a. Physical work in brushing. Technically, this means a low-viscosity paint. With present knowledge and economics, this requires water as the carrier.

      b. Minimum surface preparation. Scraping, burning, sanding, brushing and washing are physical work to be avoided.

      c. Single coat of paint. No tolerance for prime coats.

      d. Easy clean-up.

      e. Universality of application. Must perform on masonry, wood and metal.

      f. Minimum weather hazards during application.

2. Long life.

The demands made upon an exterior paint make it very unlikely that any one of the classes of pigment binder systems will be the best choice under all conditions.

A decade of history of latex polymers as the sole pigment binder in exterior latex paints has proved that a saturated, high-molecular-weight polymer will out-perform an unsaturated, low-molecular-weight polymer under ultra violet radiation in an oxidative environment.[1]

This history has also uncovered a basic adhesion problem that all latex binders share because of the physical mechanisms involved during latex film forma-tion and the requirement of high viscosities for good brushing characteristics. For these reasons, early failures of latex paints result when they are applied over such common paint surfaces as heavy, loose chalk; smooth, hydrophobic sur-faces, especially under repeated freezing and thawing; and bare wood.

The fluid alkyd or drying oil paints appear to be more suited for these sur-faces as they have a much greater ability to wet, penetrate and react with these surfaces. The oils, however, are deficient in alkali resistance and in durability.

The first marriage of these materials was to apply each separately. The oil paint was used as the primer coat and the latex paint as the top coat.[2] This ob-vious, sensible, technical solution which utilizes the strong points of each system had limited consumer success as it ran afoul of too many of the tenets of his principle of the least possible work. Other suggestions for primers, i.e. diluting latex paints with water plus additional latex emulsion,[2] the use of partial sol-vents such as toluene in the latex paint[3] and the addition of tung or other drying oils[1] had minimal success due to the consumers' resistance to using separate, dif-ferent paints and the two-coat system.

A consumer-acceptable and technically valuable merger of these materials was the use of both binders in the same paint.[4] This approach resulted in paints which overcame many of the problems that each class of binder experienced when used alone.

In Table I is shown a typical exterior, alkyd-modified, latex paint formula-tion for a vinyl chloride-acrylic polymer.[1] The performance of this polymer will be compared with an acrylic polymer[2] and a vinyl acetate polymer[3] when they are used under conditions that promote early latex paint failures.

HEAVY LOOSE CHALK

Figure 1 demonstrates the value of alkyd modification of latex paints. The two panels shown here were originally painted with a blue oil paint. The panels were then coated with a synthetic chalk composition consisting of talc, zinc oxide and titanium dioxide dispersed in water with a phosphate dispersing agent. This mixture had no binder and after it was applied by brushing, resulted in a heavy, loose coating. Over this surface on the top, lefthand portion was painted a beige vinyl chloride acrylic paint containing no alkyd. The middle sec-tion was a vinyl acetate paint containing 45% of a soya, long oil alkyd. On the

[1]Geon(R) 450X20 - B. F. Goodrich Chemical Company
[2]Rhoplex(R) AC 34 - Rohm and Haas Company
[3]Elvacet(R) 1454 - E. I. duPont de Nemours & Co.

righthand portion was painted the acrylic polymer containing no alkyd. In this and in the following panel studies the polyvinyl acetate polymer was always employed with 45% of the soya long oil alkyd. In some cases, the vinyl chloride-acrylic and the acrylic polymer are used with and without the alkyd. The same alkyd was used in all the paints and when used was at 45% of the total binder level. The alkyd was a 100% long oil soya alkyd, having a phthalic content of 16%, an acid number of 6-8 and a viscosity rating of X-Z.

All three paints on the bottom panel had alkyd modification. The A section was painted with the vinyl chloride-acrylic polymer, the B section was painted with the vinyl acetate polymer and the C section with acrylic polymer. The panels were exposed 18 months - 45° South, self-primed, in the North Central area.

The complete adhesive failure of the latex paints containing no alkyd in the upper panel graphically illustrates the value of alkyd modification for obtaining adhesion on loose, chalky surfaces. It is generally believed that the failure of latex paints on surfaces of this nature is due to their inability to penetrate the small, capillary-size pathways existing between the loosely packed pigments. This appears to be a logical supposition as penetration phenomena are a function of Van der Waals forces existing between the molecules of the liquid and the solid. The related factors involved are expressed in following equilibrium equation governing pressures in a capillary.

$$(P_1-P_2) = \Delta P = \frac{2\gamma \cos\theta}{r} \qquad (1)$$

where:

$(P_1 \& P_2)$ = Pressures on the concave and convex sides

ΔP = Pressure difference across the meniscus.

γ = Specific free surface energy of the liquid- equivalent mathematically to the surface tension.

r = Radius of the capillary tube.

θ = Contact angle between the liquid and the solid.

If θ is acute, i.e., the liquid wets the solid, pressure is positive and penetration is spontaneous. If θ is obtuse and the liquid does not wet, the solid pressure is negative and penetration is resisted.

Combining this with Poiseuille's equation for the rate of discharge out of a capillary

$$Q = \frac{\pi r^4}{8\eta l} \ (P_1 - P_2) \qquad (2)$$

where:

η = viscosity of liquid

l = length of capillary

Q = quantity of material discharged

one can obtain a rate equation for the quantity of material passing through

capillaries

$$Q = v\,dA = \frac{dl}{dt}\,\pi r^2$$

$$\frac{dl}{dt}\,\pi r^2 = \frac{\pi r^4}{8\eta l}\,\frac{(2\gamma\cos\theta)}{r}$$

$$\frac{dl}{dt} = \frac{\gamma(2\gamma\cos\theta)}{4\eta l} \tag{3}$$

The rate equation states that the liquid must wet the solid and that large capillaries and low viscosity are desirable.

Going back to the paint formulation (Table I) it is apparent that the viscosity is high (75 to 80 Kreb Stormer Units). This high viscosity is obtained through a flocculation mechanism (addition of the water soluble bridging agent hydroxyethyl cellulose) which agglomerates the particles and pigments and introduces a yield point. Therefore, a latex paint has agglomerates which can plug capillaries, a yield point and a high viscosity which would slow the rate through a capillary. Upon application of the paint, rapid withdrawal of the water (5 to 10 minutes) through the combination of wicking and evaporation increases solids with a resultant viscosity increase, further slowing down penetration. The ability of latex paint to wet the chalk is unknown but is probably in the fair to good range. In general, however, we would expect from the knowledge of the viscosity of a latex paint and equation (3) that chalk penetration would be poor. In contrast, an oil has excellent wetting ability, Newtonian and reasonably low viscosity, stays in the fluid state longer, and is not agglomerated. Materials of this nature would be expected to penetrate chalk very well. Experimentally, it has been found that at least 30% of total binder as alkyd modification is necessary to obtain the type of adhesion shown in the panels.

SMOOTH HYDROPHOBIC SURFACES ESPECIALLY UNDER CYCLIC
FREEZE THAW CONDITIONS

The relatively low-volume solids of latex paints, approximately 35-40%, results in shrinkage stresses during film formation which tend to pull the film away from the substrate. Soaps are necessary to manufacture both latexes and latex paints. The soaps can move to the interface of the paint film and the substrate. Therefore, all latex paints are faced with poor adhesion over wet, smooth, hydrophobic surfaces. These adhesion difficulties are considerably magnified under freeze-thaw conditions in the presence of moisture.

The underside of the overhang of a home is normally protected from ultra violet radiation and the washing action of rains. Paints at these sites, therefore, usually do not chalk and frequently have a dirt layer. Repainting of these areas presents a special adhesive problem of a surface composed of loose dirt over a hard, smooth, hydrophobic surface.

Field investigations using side by side comparisons of vinyl chloride acrylic-alkyd modified paint and vinylacetate-alkyd modified paint on a home in the North Central area after two years' exposure demonstrates superior performance for the vinyl chloride acrylic polymer

A closeup of the failure under the overhand of a home is shown in Figure 2.

A clean break occurs at the line of demarcation between the two paints with the left hand vinyl acetate-alkyd modified paint showing serious failure while the vinyl chloride-acrylic-alkyd modified paint has no failure. The other three sides of this house were painted with the vinyl chloride-acrylic-alkyd modified paint and no failure occurred under the eaves at any point.

It is believed that this type of a failure is a composite of several factors. Experimentally, it appears to be more pronounced in areas subject to freeze-thaw cycles when moisture is present. A possible explanation for these events is that the paint film absorbs water above the freezing point which then turns to ice when the temperature drops. The ice imposes stresses on the thermoplastic film, which at these low temperatures is becoming hard, and can cause a crack in the film. Upon further cycling, water can get beneath the film through the cracks which upon freezing continue to remove the film from the substrate. Desirable characteristics would, therefore, be low transmission of water through the paint film, low water absorption, flexibility of the paint film at low temperatures and good adhesion.

In Figure 3 are shown the effects of increasing pigment content on the moisture vapor transmission rate of different polymers. The values shown are for 4 mil unaged free latex paint films.

The M.V.T.R. is a function of both the polymer type and the amount of pigment. The rate increasing very rapidly after 35% pigment volume concentration. The polymer effect on M.V.T.R. is as expected, with the polar molecule, vinyl acetate, having the most rapid transmission rate and the less polar styrene acrylic polymer has lower M.V.T.R. rates than its polarity would suggest. This may be due to the small amount of crystallization that is suspected to occur with vinyl chloride polymers. The introduction of an alkyd as a modifier for vinyl chloride-acrylic paints (45% alkyd) reduces the M.V.T.R. approximately one half.

Meaningful water absorption data are hard to obtain because of the many factors involved. In Table II are data obtained on percent area increase when unaged latex paint films are immersed in water. It is evident that vinyl acetate polymers pick up more water than vinyl chloride-acrylic and acrylic polymers.

Later data will show that alkyd does improve the flexibility of the vinyl chloride-acrylic polymer and to some extent the acrylic polymer. It does not increase the flexibility of the vinyl acetate polymer.

The explanation for the noted difference obtained in the field appears plausible, as the experimental studies indicate that the better-performing vinyl chloride-acrylic polymer has lower M.V.T.R., lower water sensitivity, and greater flexibility than the vinyl acetate polymer.

PERFORMANCE ON BARE WOOD

For several reasons, latex paints show poorer crack resistance self-primed over bare wood than when used over oil-primed wood, particularly at high pigment volume concentrations. This effect is shown in Table III. Early cracking is a bad feature, for water can then penetrate the cracks, reduce the adhesion further and also cause more stresses on the remaining film by expanding the wood.

As has already been shown, water and water vapor will travel through latex paint films. This characteristic is both an advantage and a disadvantage depending upon the source of the water. If the water is coming from the inside of the

structure, it is a disadvantage as it causes wood swell or loss of adhesion.

The swelling of wood by water has been studied and it has been found to be a function of the wood class. In Table IV are shown the differences in the amount and rate of swelling of three wood classes. Considerable variation in swelling is noted for the different classes and also within any one class. The rate and degree of wood swelling is not uniform over the face of any panel. The rate of wood swell of summerwood is much greater than that of springwood.[5]

For the same reasons that latex paints do not penetrate chalk they do not penetrate the wood capillaries to any great extent. The latex paint, therefore, has little, if any, mechanical adhesion and acts like a free-floating film with adhesive spots where it comes in contact with the rims of capillaries in the wood or with the ridges caused by sanding and sawing of the wood. Any localized stresses due to the expansion and contraction of the wood will, therefore, be transmitted to the small section of latex film between two adhesive point contacts.

In order to reduce the damaging effects of water, it will be desirable to increase and maintain the flexibility of the polymer and/or to improve the adhesion of the polymer to the substrate.

A simple means of increasing polymer flexibility is plasticization. As paint films are thin (1.5 to 2.0 mils) and subjected to both heat and water leaching action, the loss of some plasticizers is rapid. A 35 PVC polyvinyl acetate paint plasticized with 15 PHR of dibutyl phthalate will experience a change of elongation from an original value of 125% to 20% after only 32 hours Weather-Ometer exposure. Flexibility must be obtained by internal plasticization or plasticization with non-volatile, non-extractable plasticizers.

As most paints contain pigments for decorative and economic reasons, their effect on the flexibility of a paint film was studied.

In Figure 4 is shown the effect of pigment loading on the elongation of the vinyl chloride-acrylic polymer. As the pigment content is increased, the elongation decreases. When these same paints were exposed for 500 hours in the Weather-Ometer, two effects are noted. First, in all cases the elongation decreased after Weather-Ometer exposure and second, pigmentation was beneficial to polymer films exposed to ultra violet radiation. The rapid loss in elongation of the clear film shows that this polymer is susceptible to the action of U.V. The acrylic and the vinyl acetate polymer have been shown in the literature to be similarly affected.[6] The beneficial screening effect of pigmentation is primarily due to the U.V. screening ability of the rutile titanium dioxide used in paint formulations.[7]

If flexibility of latex paint films is to be maintained, it will be desirable to keep the PVC as low as possible.

The fact that paints with lower pigment content have better crack ratings self-primed and have higher elongations than paints with high pigment content is an indication of the relationship between elongation of the films and crack rating for self-primed paints. The elongation of a paint film is a changing property dependent upon its age and its environment. In Figure 5 is shown the relationship between the elongation of free paint films that have been exposed for 500 hours in the Weather-Ometer and the crack ratings of these same paints self-primed on white pine and similarly exposed. Regardless of the polymer type, it is necessary to maintain elongations greater than 30% in the film in order for it to resist the stresses imposed upon it by the wood. This type of wood as shown in Table IV increases in area approximately 3-4% when subjected to water. The area increase is not a

uniform increase over the entire surface. If one assumes that the 30% elongation required by the film to prevent cracking failure can be equated to the change in spot areas of the wood, these results would indicate that spot sections of the wood surface may have dimensional changes 10 times as great as is indicated by the average area increase.

Another means of checking this effect is to subject the same paint film to different stresses by applying it self-primed over different wood types. This was done by applying a 25 PVC vinyl chloride-acrylic paint over the three wood types studied in Table IV and exposing the samples on a 45° South fence for 5 years at Avon Lake, Ohio. A crack rating of 8 after this period of time was obtained for the red cedar which has both a slow rate and a low amount of swelling. The white pine sample had a crack rating of 4. The yellow pine sample which has a high rate and a high amount of swelling had a crack rating of 1.

The data, therefore, indicate that to use latex paints over bare wood, it will be necessary to obtain better adhesion and better flexibility at least during the early portion of the life of the paint. The amount of flexibility is dictated by the wood surface.

Industrial practice has shown that polyvinylchloride is one of the few polymers that can be plasticized to give commercially serviceable items. Vinyl chloride polymers retain a large measure of their toughness even though they have been softened by plasticizers. It is believed that the polarity of this molecule results in interchain forces of varying strengths and that some crystallites exist. The majority of the plasticizers affect some of the interchain forces but not all, leaving the remainder to act as weak bonds between the chains to give the observed toughness of plasticized vinyl chloride polymers.

With the vinyl chloride-acrylic polymer, therefore, beneficial effects with respect to increased flexibility can be expected by plasticization with a minimum loss of toughness. It has been shown that besides flexibility, increased adhesion to the wood substrate is much needed by latex paints and that any plasticizer should be permanent.

A favored class of plasticizers for vinyl chloride are those obtained by reacting phthalic acid with a medium chain alcohol. A phthalic alkyd is obtained by reacting phthalic acid, a glycol and a drying oil.

The chemical similarity of these materials makes it appear that alkyds should be partial plasticizers for vinyl chloride-acrylic polymers. Incorporation of an alkyd should, therefore, result in improved flexibility and considerably better adhesion to bare wood. The better adhesion being due to the ability of the alkyd to penetrate the wood capillaries to a greater depth. It would, therefore, be expected that alkyd modification would result in improved performance on bare wood for those polymers that are compatible with alkyds.

In Figure 6 are shown the results obtained by alkyd modification of various polymers. All of these paints were self-primed over a yellow pine panel, a very difficult surface for latex paints. The A section was painted with the vinyl chloride-acrylic polymer, the B section with the polyvinyl acetate polymer and the C section with the acrylic polymer, all containing the same type and amount of alkyd. After 18 months' exposure - 45° South in the North Central area, the excellent flexibility of the vinyl chloride-acrylic polymer, when modified, with a partial-plasticizing alkyd is demonstrated. There are no cracks in this panel. The polar vinyl acetate polymer is apparently not effectively plasticized by the alkyd as it cracks badly on this substrate. The acrylic polymer is plasticized but

apparently loses some of the toughness necessary to withstand the repeated flexing cycles the film is subjected to as a few cracks are developing. As can be seen, the cracks which started in the polyvinyl acetate section are quickly stopped in the vinyl chloride-acrylic polymer section.

Self-priming latex paints on bare yellow pine is good for accelerated testing but is not a normal paint practice. A condition approximating this type of service, which is a common paint substrate, is the necessity to repaint old, cracked painted surfaces. Results on surfaces of this nature have been similar to those experienced on the yellow pine panel.

The apparent partial plasticization of some latex polymers by alkyds results in definite improvements in the problem areas for exterior latex paints. These advantages would be meaningless if they destroyed or compromised to any extent the strong points of latex paints. Extensive exposures have shown that latex paints have both low dirt pick-up and good tint retention which result in clean looking, painted homes.

If the plasticizing effect of the alkyd causes surface tackiness, this could result in an undesirable increase in the pick-up of dirt by the paint. In Figure 7 is shown the effect of the alkyd on the dirt pick-up of the various polymers. The panel was a red cedar panel and was exposed in an industrial area in Northern Florida. A section painted with the vinyl chloride-acrylic-alkyd paint shows only slight dirt pick-up as does the B vinyl acetate-alkyd paint section. Considerable dirt is picked up as is shown by the smudges in section C, which were painted with the acrylic-alkyd paint. The two paints which are partially plasticized by the alkyds, the vinyl chloride-acrylic and the acrylic show considerable differences in behavior to dirt pick-up.

It has been reported in the literature that acrylics undergo chain scission.[8] Our studies indicate that vinyl chloride polymers under similar conditions undergo oxidative cross linking. Typical of these reactions are the results obtained by Fade-Ometer exposure illustrated in Table V. The acrylics have a definite tendency towards tackiness in this type of test whereas the vinyl chloride-acrylics become hard. The combination effect of both heat and U.V. considerably accelerates these reactions.

The partial plasticization of the acrylic coupled with its tendency towards chain scission may be the cause of the noted aggravated dirt pick-up of this paint.

In Figure 8 is shown the effect of alkyd modification on the chalking and tint retention of the various polymers. The A section of the upper panel was self-primed with vinyl chloride-acrylic paint, the B section with the alkyd modified vinyl acetate paint and the C section with the acrylic paint. The same polymers all containing alkyd modification were painted in the same order on the bottom panel. The panel was a red cedar panel and it was exposed for two years in the North Central area. It is evident that alkyd modification has minor effects on the chalking tendency of the vinyl chloride-acrylic and the vinyl acetate polymer. It does, however, cause a considerable increase in the chalking tendency of the acrylic polymer. Rapid chalking of a tinted paint results in undesirable color changes.

CONCLUSION

Commercial experience has shown that latex paints, when compared with alkyds or drying oils, are at a disadvantage over certain surfaces. These disadvantages

appear to be related to some extent to the physical form of the binders and to requirements in formulating latex paints. Combining the two types of binders in one paint is a good solution to these problems, particularly for the vinyl chloride-acrylic polymer. The mixing of vinyl chloride-acrylic polymers with long-oil alkyds shows marked improvement in the latex problem areas without the deterioration of other important paint properties, such as color retention or resistance to dirt pick-up.

While the work reported here has dwelled to some extent on the problem areas of latex paints, it should be mentioned that excellent paint life is being obtained with latex paints. The high-molecular-weight, saturated polymers generally outperform the drying oils with respect to alkali resistance, color retention, and durability. The general performance of latex paints has resulted in a growing market for these polymers. In the past decade, latex paints have grown to the extent that they now have 25% of the exterior trade sales volume and give every indication of increasing their share of this market.

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TABLE I

VINYL CHLORIDE TINT BASE HOUSE PAINT (BFG-493)

	Pounds	Gallons
Water	140.00	16.79
Nonionic Surface Active Agent	3.00	0.34
Ethylene Glycol	20.00	2.14
Amino Methyl Propanol	4.50	0.57
Dispersant	9.00	0.98
Defoamer	5.00	0.66
Blend above and add in order listed		
Rutile Titanium Dioxide	180.00	5.14
Diatomaceous Silica	50.00	2.60
Mica	30.00	1.27
Calcium Carbonate	100.00	4.37
Mix until smooth		
(Cowles 3500-4500 ft.per min. for 10 to 15 min.)		
Water	5.00	0.60
Potassium Tri Polyphosphate	2.00	0.10
Mix 5 min. on Cowles		
2-1/2% Hydroxyethyl Cellulose Solution	100.00	11.90
Long Oil Alkyd Intermediate	96.00	11.58
Mix 5 min. on Cowles		
Wash and Reducer		
Water	20.00	2.40
Paste	764.50	61.44

Add under slow speed agitation

	Pounds	Gallons
Geon 450X20	260.00	28.26
Defoamer	1.00	0.13
Nonionic Surface Active Agent	5.00	0.56
Water or Thickener as required	80.00	9.59
	1110.50	99.98

PVC = 35%
pH   = 9.1 to 9.5 (if pH is low, adjust with AMP)
Visc. = 75 to 80 K.U.

LONG OIL ALKYD INTERMEDIATE (BFG-12273)

Blend following ingredients:	Pounds	Gallons
Long Oil Alkyd	740.00	89.16
6% Cobalt Naphthenate	4.50	0.56
24% Lead Napthenate	13.00	1.36
Mildewcide	69.00	8.66
Anti-Skinning Agent	2.00	0.26
	828.50	100.00

TABLE II

SWELLING OF UNAGED PAINT FILMS IN WATER

(Percent Area Increase After Immersion in Distilled Water
at Room Temperature)

Pigment Volume Concentration	Vinyl Chloride-Acrylic		Vinyl Acetate		Acrylic	
	30 min.	24 hours	30 min.	24 hours	30 min.	24 hours
0	2.6	8.5	3.7	27.0	4.8	11.0
25	1.1	2.1	5.8	10.5	2.1	0.5
35	0.5	0.5	3.1	3.1	3.1	1.1
45	0.5	0.5	1.1	2.1	1.1	0.5

- -

TABLE III

CRACKING RESISTANCE OF PAINTS ON WHITE PINE PANELS

(45° South - 16 Months' Aging - North Central Area)

	25 P.V.C.		35 P.V.C.	
	Self-Primed	Oil Primed	Self-Primed	Oil Primed
Vinyl Chloride-Acrylic	10	10	6	10
Acrylic	7	10	6	10
Vinyl Acetate	8	10	6	8

10 - no cracking

1 - completely cracked

TABLE IV

SWELLING OF WOOD IN DISTILLED WATER

Wood Types	Soaking Time in Distilled Water at Room Temperature		
	0.5 hrs.	2 hrs.	4 hrs.
Yellow Pine	4.80[1]	5.50	5.65
White Pine	1.80	2.30	3.50
Red Cedar	0.70	0.95	1.50
White Pine	——	5.24	——
White Pine	——	1.50	——

[1] % area increase of 2.45" x 9" x .45" unpainted panels

- -

TABLE V

FADE-OMETER EXPOSURE OF CLEAR FILMS

Type	Black Background[1]	No Background[2]
Vinyl chloride-acrylic	Yellow at 220 hours Hard and brittle at 460 hours	Slightly brittle at 1400 hours
Acrylic	Some tackiness at 300 hours Very tacky at 440 hours	Complete shrinkage at 360 hours

1 - Combination of heat and U.V. as degradating agents.
2 - Primarily U.V. as the degradating agent.
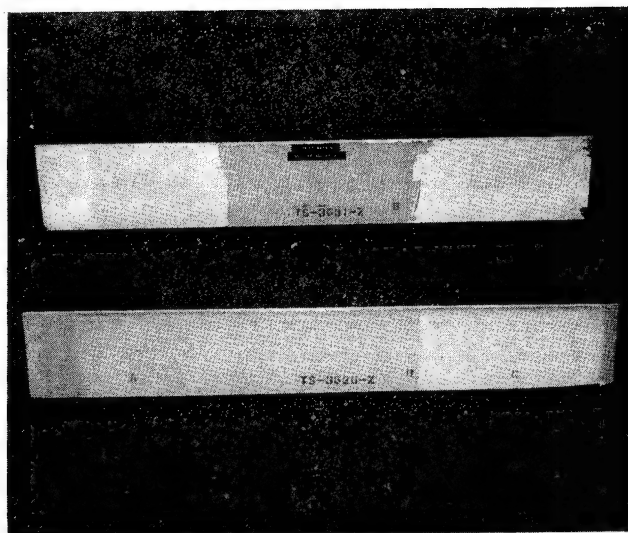
FIGURE 1: Repaint over Synthetic Chalk. Top left-hand – Vinyl Chloride-Acrylic – No Alkyd. Top center – Vinyl Acetate – with 45% Alkyd. Top right-hand – Acrylic – No Alkyd. Bottom – Same Order All Materials with 45% Alkyd.

FIGURE 2: Close-Up of Paint Under Eaves – A Smooth, Hydrophobic Surface. Left-hand portion – Vinyl Acetate – 45% Alkyd – Eave Failure. Right-hand portion – Vinyl Chloride – Acrylic – 45% Alkyd – No Eave Failure.
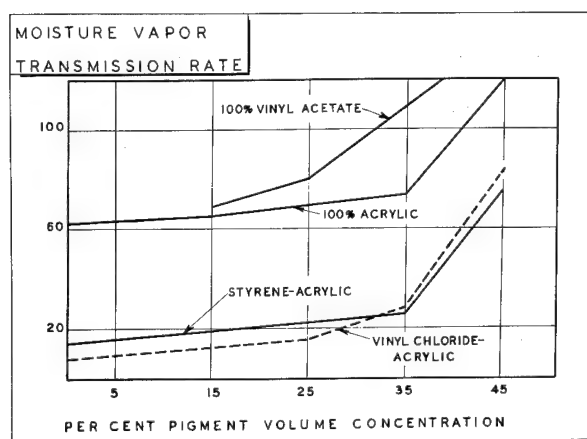
FIGURE 3: Effect of Pigment Volume Concentration on the M.V.T.R. of Latex Polymers – M.V.T.R. in Grams/100 in.^{2}/24 hours – General Foods Cabinet.
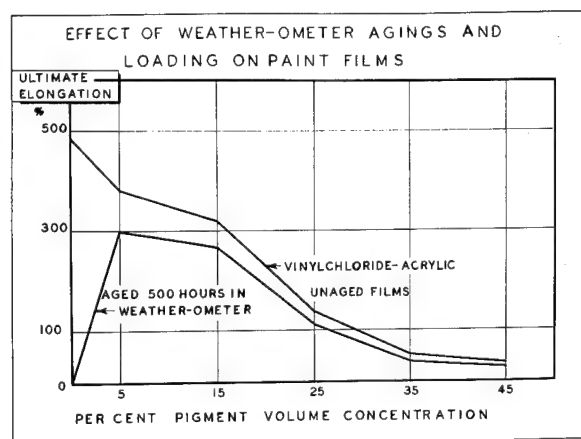
FIGURE 4: Effect of Pigment Content and Weather-Ometer Exposure on the Elongation of a Vinyl Chloride-Acrylic Polymer.
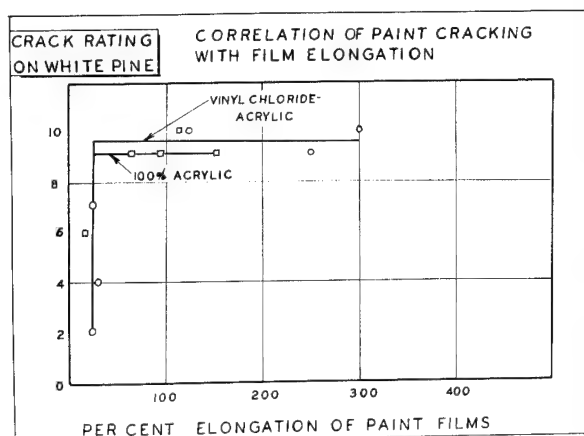
FIGURE 5: Relationship between the Elongation of Weather-Ometer Exposed Latex Paint Films and the Crack Rating of the Same Paints on White Pine Similarly Exposed.
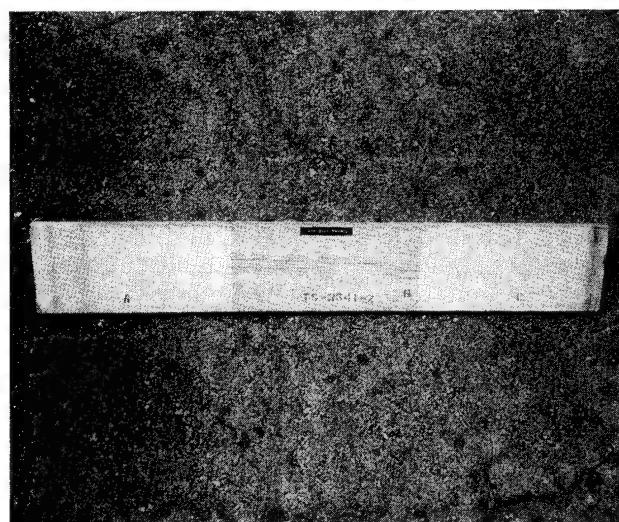
FIGURE 6: Alkyd Modified Latex Paints Self-Primed Over Yellow Pine. A — Vinyl Chloride-Acrylic Polymer, B — Vinyl Acetate Polymer, C — Acrylic Polymer.
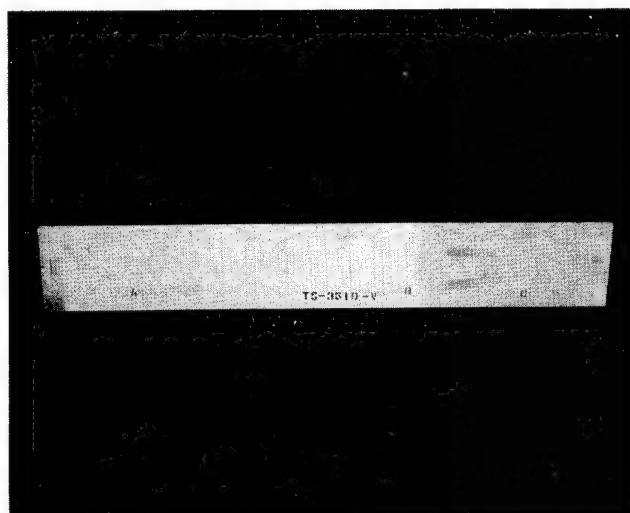
FIGURE 7: Dirt Pick-Up of Alkyd Modified Latex Paints Self-Primed Over Red Cedar. A — Vinyl Chloride-Acrylic Polymer, B — Vinyl Acetate Polymer, C — Acrylic Polymer.
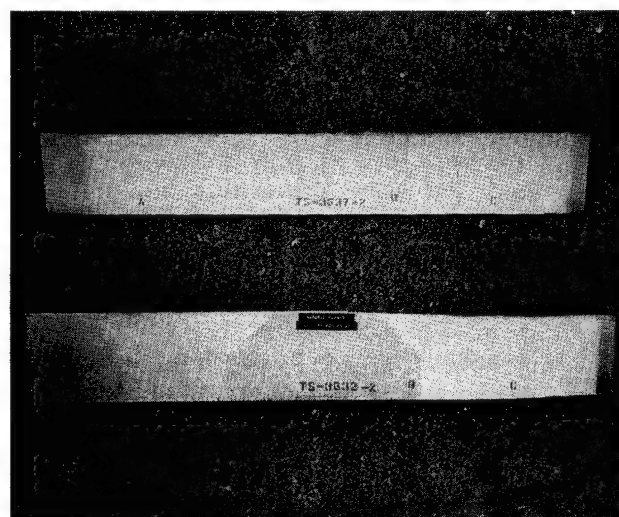
FIGURE 8: Effect of Alkyd Modification on Chalking of Latex Paints
Top Panel — A — Vinyl Chloride — Acrylic Polymer; B — Vinyl Acetate Polymer — Alkyd modified; C — Acrylic Polymer. Bottom Panel — A — Vinyl Chloride — Acrylic Polymer — Alkyd Modified; B — Vinyl Acetate Polymer — Alkyd Modified; C — Acrylic Polymer — Alkyd Modified.

VINYL FINISHES FOR COIL COATING

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INTRODUCTION

My presentation today is to cover the use of vinyl finishes for coil coating operations. Preliminary to embarking on this subject, however, I feel it is in order to briefly review the history of vinyl coatings as related to their development and acceptance in the paint industry.

Basic research and development effort with vinyl resins for use in paint films dates as far back as 1938. Within a short period following World War II, 1945-1946 to be exact, vinyl resins were being utilized in a variety of industrial coatings. At that time, solution-vinyl copolymer coatings were being used for marine finishes, transportation coatings for finishing railway hopper cars, industrial maintenance finishes and process equipment finishes.

Solution-vinyl coatings were also used by the appliance industry, to a limited degree, as far back as seventeen years ago. By 1947 vinyl coatings were being widely used as interior coatings for cans and containers. They were also used by the collapsible tube industry - and are to this day - for coating tubes used for packaging tooth paste, shaving cream, hair cream and many similar products.

Solution-vinyl coatings were introduced to the coil coating industry in 1948. The continuous coating of metal strip was not a widespread industry at that time. The few strip lines in operation were coating narrow strip largely destined for venetial blinds and awnings. The use of vinyl coatings of all types has increased along with the rapid expansion of the coil coating industry. The volume supplied has grown from a few hundred gallons per year in 1948 to several hundred thousand gallons per year at the present time.

The foregoing historical resume indicates that vinyl coatings have become extremely popular and important finishes for many industrial applications.

We shall now review the various classes of vinyl coatings relative to their properties, advantages, and importance as coil coatings. When we speak of vinyl coatings we encompass four basic coating types. The vinyl family includes solution-vinyls, organosols, plastisols and vinyl laminates.

SOLUTION VINYL COATINGS

Solution-vinyls may be defined as coatings which contain vinyl chloride-vinyl

acetate copolymer resins as the binder. Other components of the typical solution-vinyl formulation include chemical plasticizers, various stabilizers, true solvents for the resin and diluents.

The solution-vinyl coatings can be supplied in any gloss range. A wide range of decorative and durable colors can be achieved through proper pigmentation.

The basic vinyl copolymer resins present a unique combination of outstanding properties which make them well adapted to a variety of surface coating applications.

Some of the inherent outstanding properties are:

1. Ease of application - Solutions of vinyl resins in suitable solvents can be applied by roller coating, dipping, spraying, curtain coating, flow coating or brushing.

2. Chemical Inertness - Vinyl coatings are not attacked at normal temperatures by practically any strength of alkalies or mineral acids. The coatings are insoluble in alcohols, greases, oils and aliphatic hydrocarbons. They are, however, soluble in ketones, esters and aromatic hydrocarbons.

3. Excellent adhesion, toughness and flexibility - Properly cleaned and treated metal sheets or strip coated with vinyl coatings can be lock-seamed, crimped, drawn, roll formed, or stamped with little or no marring or fracturing of the film.

4. Resistance to aging - Vinyl copolymer coatings maintain their original hardness and flexibility upon aging. This makes them well adapted to latent post-forming or fabricating operations.

5. High water resistance - Binyl copolymer coatings possess a low moisture vapor transmission rate and low moisture absorption rate.

6. Resistance to weathering - Properly formulated and properly pigmented vinyl coatings exhibit excellent durability on exterior exposure.

7. Water-white color - The good clarity, high refractive index, and light color of the vinyl copolymer resins make possible clean whites and tints in pigmented coatings and brilliant films in clear finishes.

The properties enumerated above place a high demand for vinyl finishes for coil coating. Solution-vinyls are currently being used to coat aluminum and steel strip up to sixty-six inches in width. The coating speeds on the modern continuous strip coating lines often run as high as three hundred feet per minute. The solution-vinyl coatings fuse to the substrate on short, high temperature bake schedules. Schedules of sixty seconds at 450° to 500°F. ambient temperature are quite common.

Although all of the film properties previously mentioned are important, two stand out above all others as the reason for the extensive use of solution-vinyl coatings. They are:

1. The high degree of film flexibility and distensibility which allows

vinyl coated stock to withstand the more difficult forming and
fabricating operations. The advantage of maintaining flexibility
on aged strip is also an important attribute.

2. The overall excellent weathering properties of solution-vinyl
   coatings.

Both of the mentioned properties are important. I would like, however, to
enlarge somewhat on the exterior durability or weathering aspect. This is most
important, since estimates from the coil coating industry have indicated that 65
to 75% of the coated strip is destined for exterior exposure.

The prefinished exterior products include aluminum house siding, steel resi-
dential siding, aluminum awnings, curtain wall, mobile home sheathing, gutters and
downspouts, sluminum roof shingles, under eave soffit panels and other building
components. When exterior exposure resistance is a prime requisite of the end
product, great care must be exercised to recommend and use the very best coating
for that purpose.

What do we mean by good exterior exposure resistance? How do we define this
property? In order that a coating be in this category it must possess the follow-
ing characteristics:

1. Excellent adhesion to the substrate and the ability to retain
   such adhesion.

2. Maximum chalk resistance in tints and colors. Self-cleaning
   by slight chalking in white.

3. Maximum fade resistance in tints and colors.

4. Resistance to mildew growth.

5. Good corrosion resistance (properly prepared substrate is neces-
   sary in this instance).

6. Good resistance to industrial atmospheres, acid and alkaline
   fumes.

7. Film must not have an affinity for excessive dirt collection
   and retention.

8. Film must have slow-to-moderate erosion (controlled) rate to
   assure long film life at relatively low film thickness. (Average
   applied film, 1 mil dry.)

Properly formulated solution-vinyl coatings qualify in all the above exterior
requisites. We can truly consider them as time-tested, time-proven finishes
based on actual long-term exterior exposure background. On aluminum house siding
we have seventeen years' exposure experience in white and up to fourteen years'
experience in colors. Periodic field surveys of sided homes in various geographic
areas have indicated excellent performance.

As a supplement to field exposure work, solution-vinyl coatings have been
thoroughly evaluated in the laboratory under many tests specifically designed to
measure durability. Table I indicates performance under several evaluation pro-
cedures.

ORGANOSOL COATINGS

Organosols are vinyl dispersion coatings. They are suspensions of very finely divided vinyl chloride type resins in organic liquids which are not capable of dissolving the resin at room temperature. In an organosol at least part of the suspending phase consists of volatile liquids. The typical organosol formula would contain the high-molecular weight vinyl chloride resin, plasticizer, volatile thinners, stabilizers, pigments and extenders.

As with the solution-vinyl coatings, the properties of an organosol can be varied by the amount and type plasticizer used. The plasticizer content may be in the range of 1% to 40% depending on the final film properties desired. Very often a mixture of various plasticizers is employed in order to achieve specific end properties or coating characteristics.

Being dispersion type coatings organosols do not become continuous or homogeneous coating materials until they are subjected to heat. The dispersants; namely, plasticizers, and volatile thinners, dissolve and fuse the resin into a continuous coating material when certain temperatures are achieved. This is often referred to as the "fusion temperature". In most instances a minimum metal temperature of 360°F. must be obtained to effect fusion and film formation. The organosol need only reach the fusion temperature momentarily for proper film formation.

Organosol coatings have been used as coil coating finishes to a limited degree in the last ten years. They have not been as widely used as the amine-alkyd, solution-vinyl, or acrylic type coatings. Organosols have been adopted rather slowly because of certain problems encountered in the field.

Color control, particularly in white, was difficult to achieve due to heat sensitivity and stabilization problems. Rather severe metal marking and burnishing tendencies were encountered in the low gloss films. Exterior exposures on some of the early organosol coatings indicated heavy dirt accumulation and dirt retention. The latter condition was due to migration and exudation of the plasticizer which then became orientated on the surface of the film and held dirt.

The problems mentioned above are nothing more than "growing pains". As new type coatings are brought into use, certain problems always become apparent. Steady, diligent and determined research and development effort can generally alleviate the problems. This has been true with the organosol coatings, and we now have excellent performing, durable coatings of this class. The discoloration problem has been eliminated by proper stabilization. Metal marking and burnishing - although still somewhat of a problem - has been minimized by testing and selecting various extender pigments. The proper selection of plasticizers has greatly minimized the problem of dirt collection on exposure.

One and two-coat organosol coating systems are being successfully used today on several coating lines.

The organosols embody all the exceptional film properties previously outlined for the solution-vinyls. They exhibit exceptional film hardness, adhesion, and flexibility. When properly formulated and pigmented, these films possess all the properties necessary for good exterior durability. They are, therefore, suitable for finishing metal siding, curtain wall, partitions and the like.

Perhaps the greatest advantage of the organosol film is its extreme flexibility and distensibility. They are more flexible than the solution-vinyl type. As an example, the two-coat (special primer and topcoat) organosol low gloss system

will withstand a reverse impact sufficient to fracture the metal (approximately 40-60 inch pounds on 0.24 aluminum) without film crazing or loss of adhesion. Organosol coated aluminum stock has been embossed with severe pebble-grain or striated patterns and yet exhibit excellent film integrity. This makes the organosols very well adapted to embossed type products as aluminum residential siding, under-eave soffit panels, aluminum roof shingles and aluminum rain carrying equipment. They certainly should be used to finish those end products requiring difficult forming operations as seaming, embossing or stamping.

As in all manufacturing and business operations, some place along the line the economic factors must be considered. In precoating strip and sheet, finishing cost becomes an important facet of the total operation. The competitive nature of the strip coating market today necessitates a close look at unit finishing cost figures. Organosols are generally formulated to have high volumetric solids, thereby providing exceptional coverage per gallon and low unit finishing cost. The volume solids of a white organosol will generally be in the range of 53 to 55%. Various colors will have somewhat lower volume solids, but will still be in the vicinity of fifty per cent. Unit finishing cost as low as .55 to .60 per square foot at 1 mil dry film have been realized with organosol coatings. This is an outstanding feature of an organosol, since it provides the exceptional durability and performance of a solution-vinyl coating at much lower unit finishing cost.

PLASTISOL COATINGS

Plastisols, like organosols, are dispersion coatings based on high molecular weight vinyl chloride homopolymer resins dispersed in a plasticizer. They also contain small quantities of stabilizers. Plastisols generally range from 97 to 100% volume solids, and do not contain volatile solvents as do the organosols. Due to the high solids and lack of solvents, plastisols can be applied in heavy films and fused with heat without the fear of film discontinuity due to solvent popping.

Plastisols are two-coat systems. They require the use of special primer to achieve proper bond to the substrate. The plastisol primer is a most important link to satisfactory performance of the total system. The properties required of a plastisol primer are as follows:

1. Excellent adhesion to the substrate (properly phosphated or chromate treated metal).

2. Excellent intercoat adhesion with the plastisol topcoat.

3. The ability to maintain adhesion to the substrate, as well as film intercoat adhesion upon aging under conditions of exterior exposure.

4. The ability to withstand fabrication by brake forming, roll forming, stamping or deep drawing.

Plastisol primers are formulated from a variety of polymer resins. Some of the major resins used are acrylics, phenolics, epoxies, polyesters and urethanes. Very often combinations of the above resins are employed to impart specific or desirous properties to the primer. Plastisol primers are applied at low film thickness (.1 to .2 mil dry), and respond to short high bake schedules as 60 seconds at 500°F.

Plastisols topcoats are applied at high film thickness. Depending upon the end use, the dry film thickness can range from four mils to fifteen mils. Heavy films are employed to enable the film to be embossed into a variety of patterns. Some of the most popular embossed styling includes wood-grain, pebble grain, linen or leather patterns. Embossing equipment can be installed in the modern continuous coil coating line.

Plastisols can also be formulated to provide a striated or wood-grain pattern without resorting to an embossing operation. The rheological properties of the plastisol can be adjusted to provide various striated patterns at the roller coating head, and prior to the baking operation. The striated plastisol coating has become very popular as a finish for metal residential siding.

The film properties of a plastisol can be varied to a considerable degree. Plastisols can, in fact, be formulated over a much wider range of physical properties than most other coatings. Plastisols, in general, also possess several inherent properties which place them above many other coatings in terms of performance. The outstanding properties or areas of performance are enumerated below:

1. Exceptional adhesion (over properly treated, primed metal).

2. Excellent film flexibility, forming and fabrication properties.

3. High abrasion and scuff resistance.

4. High chemical resistance.

5. High corrosion resistance (industrial atmospheres).

6. High grease and oil resistance.

7. Excellent weatherability - when properly formulated.

Plastisols can be formulated to have film hardness equivalent to solution-vinyls and organosols. The plastisol film generally contains a higher level of plasticizer than the solution-vinyls or the organosols. The plasticizer level can have a profound effect upon film characteristics. For example, a decrease in plasticizer content will increase the tensile strength and hardness of the film. By manipulating the plasticizer content it is possible to achieve a given film hardness, and yet maintain adequate flexibility, elongation, and tensile strength for fabrication. Even at a low plasticizer level, the elongation of a plastisol film is 180%. This is actually beyond what is needed for any post forming operation.

The use of plastisols in the coil coating industry has been rather limited when compared to the other major finishes. Plastisol coated coil and sheet has been used to fabricate numerous commodities. The U. S. Steel Company was an early and large supplier of plastisol coated steel for the general market. The embossed plastisol coated stock was formed into many products as T.V. cabinets, chair seats, room coolers, luggage, automotive and aircraft interior trim. Several other coil coaters are now equipped to supply plastisol coated metal.

The largest and most recent growth area for the use of plastisols is the finishing of metal for building components. Three or four years back, plastisols were not recommended for exterior use. This was largely due to the lack of broad experience as an exterior coating. Exposure studies also indicated that conventional plastisol films had a propensity to collect and hold dirt on the film

surface. This, of course, would result in a very unsightly condition within a short period of time.

Within the last two years, concentrated research and development effort on plastisols has resulted in an exceptional product for exterior use. The dirt collection tendency has been reduced to an acceptable level. This has been achieved through selection of the proper plasticizer and maintaining proper plasticizer level. The film hardness of an exterior plastisol is set at a higher level than conventional interior types. This additional hardness also helps preclude dirt pick-up and retention.

Plastisols are now supplied commercially to the coil coating industry for finishing aluminum and steel residential siding, curtain wall and building parttions. Plastisols, like organosols, have a low unit finishing cost. This allows them to be applied at a much greater total film thickness, with material cost only slightly in excess of the solution-vinyl coatings. The higher film thickness (3 to 4 mils dry) offers greater corrosion resistance, weatherability and extended film life. This is a definite advantage for both residential siding and commercial and industrial building components.

Based on our present knowledge regarding the weatherability of vinyl coatings in general, we can project a film life of twenty-five to thirty years for a plastisol. This, of course, would depend upon proper formulation of product, proper application (3 to 4 mils dry) over a suitable substrate.

Plastisols will require very little maintenance. They possess excellent fade and chalk resistance on exterior exposure. They also have the advantage of being easy to clean, in the event periodic cleaning is required due to location of the installation. I have reference here to homes or buildings that might be located in industrial areas or other dirt-laden atmospheres.

It is inevitable that plastisols will become important and widely used finishes in the coil coating industry.

VINYL LAMINATES

I am certain the Society of Plastics Engineers has had presentations in the past covering vinyl laminates. I do not profess to be an authority on this subject, as it lies somewhat beyond the realm of paint technology. Vinyl-metal laminating is a specialty field which is covered by competent concerns that supply self-supporting, calendered vinyl films.

Laminating equipment can be installed into a modern coil coating line. Many lines of this type are currently in operation. My discussion on vinyl-metal laminates will be brief; however, in a concise manner I will cover the laminating operation, properties and advantages of the system, and the major uses for the product.

Chemically, the vinyl sheet used for laminating is very similar to a plastisol coating. The typical vinyl calendered sheet contains the high molecular weight vinyl resin, plasticizers, fillers, colorants, pigments and stabilizers. The sheets are produced by a calendering technique and range in thickness from four to twenty-five mils.

The properties of the sheet can be varied considerably, as with the plastisols, by selection of ingredients, plasticizer level and type stabilizers used.

The end use or ultimate product involved should be taken into consideration during the formulation stage. In general, vinyl sheet can be formulated to have excellent film flexibility, stain resistance, abrasion resistance, resistance to acids, and alkali, electrical resistance and other properties imparted by the vinyl resin group.

A most important requirement for the successful laminating of vinyl sheet to metal is a very clean surface. The typical five stage cleaning and phosphatizing system employed in coil coating lines is recommended.

When the metal has been properly cleaned and treated, an adhesive is applied by roller coating. In terms of dry film, the adhesive is applied at 0.3 mil to 0.6 mil in thickness. The amount of adhesive applied depends upon the type used. The adhesive coated metal is then heated to 400° to 410°F. At the exit end of the oven the vinyl sheet is brought into contact with the adhesive coated metal strip. The bond is secured by passing the vinyl-clad strip through laminating, wringer-type or nip rolls. Directly behind and following the nip roll, the vinyl clad metal is cooled with cold water.

The vinyl-metal laminates embrace a wide selection of colors, embossed patterns and textures for the designer. They offer the advantage of providing a wider range of high-styling in colors, and combination of colors, than the fluid type plastisol coatings. The vinyl-metal laminates are, however, considerably more expensive in terms of both material and processing cost as compared to fluid plastisol coated metal.

Vinyl-metal laminates are made to withstand severe forming and fabricating operations. They have been widely used to fabricate many end products. Some of the more prominent commodities are luggage, camera housings, office equipment, school equipment, T. V. cabinets, automotive radio cabinets, lighting fixtures, automotive dash boards and interior building trim. New product markets are continually being found for both plastisol coated and vinyl-laminate coil stock.

In conclusion, we can predict that vinyls will continue to be important and widely used coatings in the coil coating field. They will always have a place in this growing industry because of their many advantageous properties and their versatility. Coating technology, as all sciences, will continue to advance. We will hear of new type coatings as silicone-alkyds, polyesters, silicone-polyesters, polyvinyl fluoride coatings and various combinations of these coatings. All of those enumerated above have merit and will become important coil coating products. Yet, they will have some catching up to do to match vinyls in line performance, exterior exposure background, extensive field use, public appeal and overall versatility.

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TABLE I

Chemical Resistance	10% H_2SO_4, 10% HCl, 10% Na OH 16 Hours - NO CHANGE
Weatherometer Resistance	National Carbon Arc Weathering Unit - 6000 Hours NO COLOR CHANGE - NO CHALKING
Dry Heat Resistance	100% Overbake (temperature constant) - NO SIGNIFICANT VISUAL CHANGE
Salt Spray Resistance	20% Salt Concentration at 97°F. - 2,000 hours NO CHANGE - NO CORROSION OR CREEPAGE FROM SCRIBE LINE
Forming Characteristics - 77°F.	Impact Resistance: 7 Gloss - 20"/lb. - No film fracture 30 Gloss - 30"/lb. - No film fracture 90 Gloss - 40"/lb. - No film fracture Bend Flexibility: 7 Gloss - 1T Bend @ 90° O.K. 30 Gloss - 1T Bend @ 135° O.K. 90 Gloss - 1T Bend @ 180° O.K.
Humidity Resistance	100% Relative Humidity (Dew Point) at 100°F. - 8000 Hours NO CHANGE
Water Immersion - 77°F.	1000 Hours - NO CHANGE
Abrasion Resistance (2 mil dry film)	Taber Abraser - CS-10 Wheels 1000 Cycles 1000 Gram Weight Load. Loss 45-50 milligrams EXCEPTIONAL (low loss)
Cass Corrosion Test	5% Salt Concentration Trace - Copper Chloride pH 3 Temperature 120°F. 100 Hour test, Slight blistering and creepage at scribe line. RESISTANCE GOOD

NOTE:

All tests conducted on 3003 H14 Aluminum Alloy treated with Bonderite
#721. Gauge .020. Dry film thickness 1 mil - bake schedule 90" @ 420°F.

FORMULATING PARAMETERS FOR ORGANOSOL METAL FINISHES

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INTRODUCTION

Organosols that are used to produce relatively thin coatings, 1 mil or so, are very different in their composition and in their performance requirements from other organosols, plastisols, or non-vinyl liquid finish systems. They must perform as paints, yet they require much of the technology of plastisols for formulating.

First, the term organosol should be defined. Generically, it denotes a dispersion of a vinyl resin in a liquid ingredient; and a portion of that liquid is volatile. Beyond this, organosols that are used for thin decorative and protective finishes must contain a large amount of pigment, to provide the opacity and durability that is required.

These organosols may be considered to be of two types, depending on their application method. These two types are one-coat organosols and two-coat systems. The major differentiation between them is that one-coat organosols contain an ingredient, usually a soluble vinyl resin, to promote adhesion. The two-coat organosols, on the other hand, do not necessarily contain any dissolved polymer; and, consequently, they require a primer to bond them to the substrate.

Both types of organosols offer advantages over other types of thin coatings in that they use as a major portion of the binder the relatively low cost vinyl plastisol type (paste) resins. In addition, this resin is used in suspension, rather than in solution, which results in a lower thinner requirement. Also, these finishes have the inherent toughness and excellent formability of the thermoplastic vinyl.

A brief comparison of some of the finish systems now in use and their characteristics are shown in Table I. As can be seen from this table, organosols offer the desirable combination of outstanding properties and low cost.

The two types of organosols, one-coat and two-coat, are prepared in a similar way; but they differ in their composition and in the technology of their formulation. Consequently, to simplify this discussion, the two types of organosols will be treated separately.

TWO-COAT ORGANOSOLS

As was mentioned, two-coat organosols, like plastisols, require the use of an

adhesive primer. There are many good primers available for this, and they can be obtained from a large number of sources.

COMPARISON TO PLASTISOLS

Two-coat organosols are similar to plastisols in that they are made from paste (plastisol type) resin, stabilizer, pigment and plasticizer. They are different from plastisols, though, since the pigment level must be quite high, for opacity; the plasticizer level is low, for hardness; and a volatile thinner is used as a portion of the liquid component.

COMPARISON TO PAINTS

Different from conventional paint finishes, the resin binder in an organosol is in suspension, rather than in solution. As a result, the thinner demand of this high molecular weight thermoplastic is quite low; and it behaves almost as a suspended pigment until it is fused during the baking of the finish.

USE OF SURFACTANTS

Since the resin is in suspension, it does not adsorb onto the pigments in the wet organosol, and some other means must be used to promote pigment wetting. One way to do this and to prevent pigment flocculation is to add surfactants to the pigment grind or to the organosol. However, since paste resins contain surface active materials themselves, surfactants must be chosen with care. Table II illustrates this point (compounds 4 and 5); and it shows one good surfactant system for use with Geon resin 120X203 (compound 6).

SOLVENTS

An additional consequence of the polymer being in suspension is that the rheology of the organosol can be greatly affected by the choice of thinners. Strong solvents, such as ketones, can attack the resin. This causes the resin to swell, and the viscosity of the organosol will increase through a decrease in the volume fraction of the liquid. On the other hand, thinners such as aliphatic hydrocarbons, which are non-solvents and non-dispersants, can cause flocculation of the resin, which results in high viscosity and false body. The best results are obtained by using a balanced thinner system. An example of this is the 1:1 mineral spirits: DIBK system used for the compounds in Table II.

CRITICLE PIGMENT VOLUME CONTENT

Another effect that appears to be due to the resin being in suspension rather than solution is that the critical pigment volume content occurs at a relatively low level. Ultimate elongation has been used to determine the critical PVC of paint films.[1] This was done for organosols of the base formulation shown below. Two resins, one of fine particle size (average particle diameter = 0.15μ, monodisperse) and one of larger particle size and wider particle size distribution (average particle diameter = 0.35μ, range 0.09μ to 0.90μ) were used to determine the effect of particle size on CPVC.

Test Formulation:

Resin	100
DOP	15
Admex 746	10
Thermolite 119	3.5
Ti-Pure R-610	varied
2:1 Span 80: Renex 650	1.5% of Pigment
3:1 Mineral Spirits: DIBK	as needed

Figure 1 shows the results of this study. In both cases, the critical pigment volume content occurs at about 12% PVC. This is well below the 40% to 55% that would be expected for systems in which the binder is a dissolved polymer. This graph also shows that the rate at which changes occur at CPVC is dependent on the particle size of the resin. The larger particle, polydisperse resin shows a sharper inflection than does the smaller particle, monodisperse resin; but the CPVC occurs at about the same pigment level with both resins.

The low pigment level at which CPVC occurs has several implications. It means that, using only dispersed resin, it is difficult to prepare highly pigmented (20% to 25% PVC) organosol coatings that have high gloss or low permeability. This and the fact that this resin is not adsorbed onto the pigment mean that coatings made from this type organosol have poor resistance to metal marking.

ONE-COAT ORGANOSOLS

Many of the problems mentioned with regard to the two-coat organosols can be solved by using a dissolved resin as a portion of the binder. The resins most commonly used for this are the carboxyl modified vinyl chloride-vinyl acetate copolymers. Although they require more solvent, they offer many advantages. These polymers will raise the CPVC value because they are dissolved, and they will adsorb onto the pigment. This means that higher pigment loadings can be used without sacrificing gloss and impermeability, and resistance to metal marking can be improved. If a large enough portion of this dissolved resin is used, a one-coat system can be made that has adequate adhesion for most applications and that will withstand most forming operations.

SOLVENT SYSTEMS

To use a dissolved vinyl polymer with a dispersed vinyl polymer and to have good viscosity stability requires some care in formulating. One area in which this is particularly important is the selection of the solvent system. It is necessary to keep the one resin in a stable solution without swelling the other resin, which is in suspension. If the solution is unstable, there will be an appreciable thixotropic increase in viscosity on aging; and, if the solvent system is too strong, the swelling of the suspended resin will also cause viscosity to increase on aging.

Although it is not likely that a stable solution can be achieved simultaneously with no swelling of the suspended resin, a careful balance of solvent, dispersant and diluent can approach it quite closely. Table III shows several typical solvent systems; and it illustrates the effects that result from changing the solvent balance. In this case, Isophorone is the solvent, aromatic solvent 100 is the dispersant and mineral spirits is the diluent.

As can be seen by formulation number 5, a properly balanced solvent system will give good viscosity stability. By comparison, a commonly used system (formulation number 2) gives much poorer viscosity stability.

SURFACTANT

The combination of the solvent system and the fact that a dispersed resin is used can cause a non-wetting effect in films cast from organosols similar to formulation 5 of Table III. This is not truly non-wetting; and it resembles fisheyes, but on a much larger scale.

This non-wetting was attributed to the Marangoni effect as illustrated in Figure 2. What happens is that a nucleating particle, such as a resin agglomerate allows evaporation to occur at a small site. This creates a localized area of low surface energy. The surrounding surface then retracts toward a more favorable equilibrium position, withdrawing the wet film through viscous coupling.

It was found that surfactants, such as those used to wet the pigment in two-coat organosols, alleviate this problem; but they also cause a significant loss in adhesion. One material, Antifoam Q, is effective in preventing the non-wetting, and it does not have any adverse effect on adhesion at the level needed for this purpose. Figure 3 shows the effect and the result of using 0.1 phr of Antifoam Q.

STABILIZATION

The use of a carboxyl containing polymer presents another factor that must be taken into account. This is the selection of a stabilizer. The normal stabilizers for use with plastisols are reactive with the carboxyl groups on the solution vinyl resin. They can cause gelation of the solution or, at least, a large increase in viscosity. A few stabilizers, however, appear to be much less reactive than the rest. Two examples of these are liquid tin mercaptide and lead sulfate as illustrated in Table IV.

What has happened with the barium-cadmium and the barium-cadmium-zinc stabilizers is they have crosslinked the solution polymer through its carboxyl groups, creating a partial gel network. Most stabilizers will have this same effect.

EFFECT OF FINENESS

In preparing an organosol, there is one factor that is of importance. This is the fineness of grind, or degree of dispersion, of the paste resin. Although the average ultimate particle of a paste resin is usually about 0.012 mils (0.35μ), all commercially available resins are agglomerated to particles of 1.75 mils (42μ) or larger.

To produce an organosol that will give an impermeable or glossy finish at one mil, these agglomerates must be reduced in size. This may be done with a roller mill, a pebble mill, a sandmill, or a high speed dissolver type mixer. The results of pebble milling an organosol to successive fineness and the effect on gloss are shown in Table V.

This shows that the gloss of an organosol coating, and, consequently, the smoothness of the film, are dependent on the fineness of grind of the paste resin. The formulation used here is the same as was used in the thinner study, and is

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shown at the bottom of Table III.

SUMMARY

[Organosols can be classified in two types, one-coat or two-coat. The main dif-
ference between the two is that the one-coat system contains a dissolved resin to
promote adhesion to the substrate while the two-coat organosol does not.

Factors to be considered in formulating two-coat organosols include lack of
adsorption of the polymer onto the pigment, selection of surfactants for pigment
wetting, thinner balance, and pigment level. The lack of adsorption by the resin
requires the use of surfactants for pigment wetting.] The selection of these
surfactants is, in turn, affected by the presence of surface active materials on
the resin. Because the resin is suspended, rather than dissolved, thinners must be
selected to be active enough to suspend the resin and to prevent flocculation but
not so active as to swell the resin particles. Also, as a consequence of the resin
being suspended, the critical pigment volume content of an organosol occurs at a
low pigment level, in the area of 12% to 14% PVC.

[Additional factors must be taken into account when formulating one-coat organo-
sols because of the solution resin used. These include solvent selection, surfac-
tant choice, stabilizer use, and fineness of grind.] Solvent balance is critical be-
cause it is necessary to have a stable solution of one vinyl polymer without swell-
ing the other vinyl resin which is in suspension. A surfactant may be necessary to
prevent non-wetting of the film, but it must be one that will not hurt adhesion to
the substrate. Stabilizers must be selected with care, since most common stabiliz-
ers for vinyls will cause at least partial gelation of the solution of the carboxyl
containing vinyl resin. Fineness of the paste resin grind is important because it
determines the gloss and the uniformity of the resulting film cast from an organo-
sol.

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TABLE I

COATINGS COMPARISON

Type of Coating	Character, Thermoplastic	Formability	Durability	% Solids, Volume	Approx. Selling Price, $/Gallon	Approximate Cost of Coating $/100 ft² mil (not including application cost,$)
Solution Vinyl	Thermoplastic	Excellent	Excellent	20-25	4.00	.90-1.00
Alkyd	Thermoset	Poor-Fair	Good	42	3.85-4.00	.60- .70
Acrylic	Thermoset	Fair	Excellent	45	4.70-5.00	.75- .80
Vinyl Alkyd	Combination	Good	Good	35	4.25	.85- .90
2-Coat Organosol	Thermoplastic	Excellent	Very Good	50	5.40	.70- .75
1-Coat Organosol	Thermoplastic	Excellent	Excellent	33	3.75-4.00	.75

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TABLE II

SURFACTANT EFFECTS

	1	2	3	4	5	6
Surfactant	None	Control 2F-SB	Span 80	Renex 650	Atlas G-3300	2 Span 80 1 Renex 650
Type	———	Soya Lecithin	Sorbitan Monooleate	Polyoxyethylene Nonionic	Ionic	———
Brookfield RVF Viscosities (poises)						
Pigment Grind						
Initial V'2	860	304	340	16	4.6	260
V'4	600	171	205	11	4.2	194
V'10	384	81	110	7.5	3.4	92
V'20	296	47	72	5.6	2.6	63
Yield	1040	500	540	17	1.6	260
Organosol						
3 Day V'2	1060	482	980	416	1015	220
V'4	850	261	532	253	985	136
V'10	407	115	228	123	645	70
V'20	220	63	120	71	375	42
Yield	840	880	1800	650	120	340

Test Recipes:

Pigment Grind:
(Pebble Mill)

Titanox RA-NC	153
DOP	20
Admex 746	10
Thermolite 119	3.5
Mineral Spirits No. 10	10
Diisobutyl Ketone	10

Organosol:
(Delta Mix)

Geon resin 120X203	100
Pigment Grind	208.8
*Mineral Spirits No. 10	20
*Diisobutyl Ketone	20

*Mill Wash

TABLE III

EFFECT OF THINNER COMPOSITION ON VISCOSITY

Solvent System	1	2	3	4	5
Isophorone, %	10	15	20	25	35
Aromatic Solvent 100, %	90	85	80	75	50
No. 10 Minteral Spirits, %	—	—	—	—	15

Brookfield RVF Viscosity (Poises)

20 RPM	1	2	3	4	5
One day	111	68	49	42	—
One week	115	71	55	50	42
2 weeks	303	136	90	81	42
4 weeks	900	460	222	192	57
4 week/1 week	7.8	6.5	4.0	3.8	1.35
Increase in viscosity 1 week to 4 weeks, %	680	550	300	280	35

Test Formulation:

Geon resin 120X203	50
*Geon resin 443	50
DOP	30
Epoxidized Oil	5
Thermolite 31	1
Ti-Pure R-610	132
Solvents	300

*in solution

TABLE IV

STABILIZERS - VISCOSITY EFFECTS

Stabilizer	None	Ferro 6V6A	Thermolite 116	Thermolite 31	Dyphos	Mac Gregor #830
Type	——	Liquid Ba-Cd-Zn	Liquid Ba-Cd	Liquid Sn-SH	Dibasic Lead Phosphite	Lead Sulfate
Level (phr)	——	3.0	3.0	2.5	15.0	15.0
One Week Brookfield RVF Viscosity (poises)						
V'_2	26	190	475	36	100	68
V'_{20}	24	140	325	30	66	48

TABLE V

GLOSS DEPENDENCE ON FINENESS

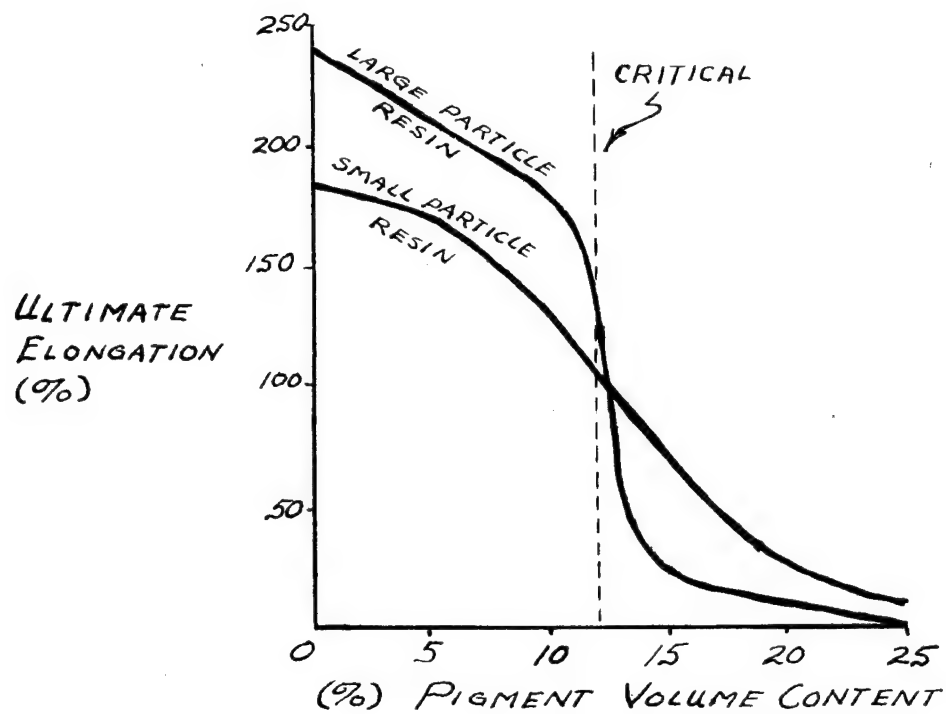| Fineness (Hegman N.S.)	60° Gloss
5.0	24
5.5	36
5.75	40
6.25	45
6.75	50
7.75	55

FIGURE 1: CPVC Determination
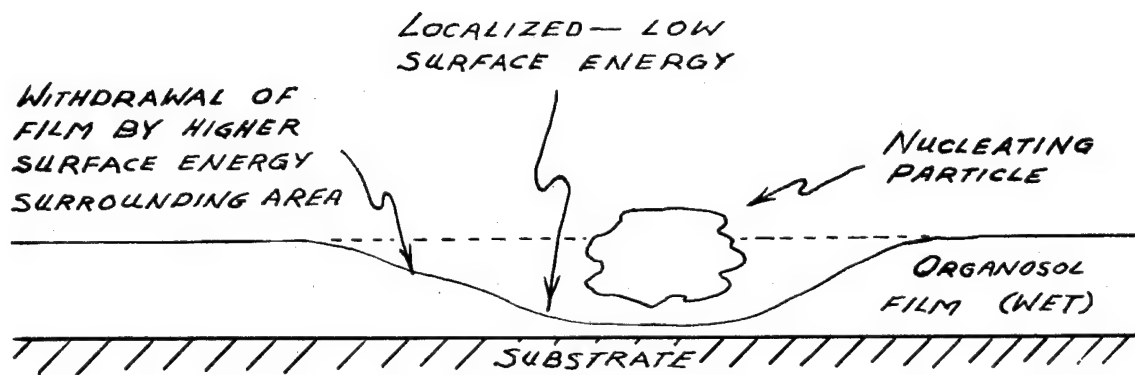

FIGURE 2: The Marangoni Effect
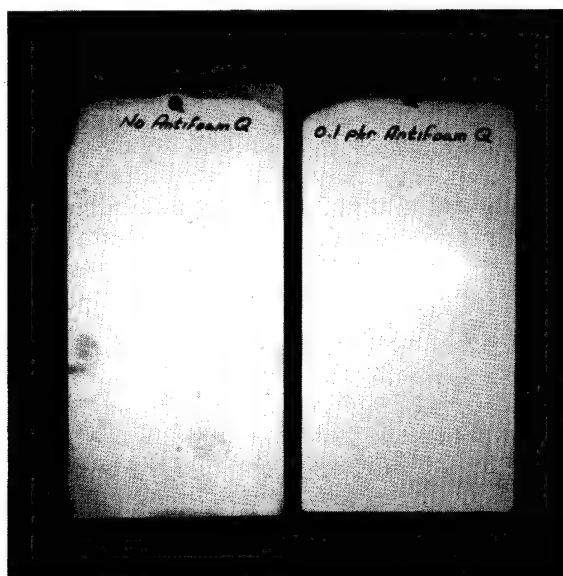
FIGURE 3

VINYL AND THE COIL COATINGS INDUSTRY

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ABSTRACT

[This paper discusses the formulating problems posed by the coil coating tech-
nique; what part solution vinyls, organosols and plastisols play in solving these
problems; and what the suppliers to the vinyl formulator might do to help expand
the use of vinyl in the coil coating industry.]

INTRODUCTION

Coil coating, although it can be simply described as another method of apply-
ing coatings, is really more than that; coil coating is an idea. The idea simply
stated is this: decorative and/or protective coatings can be applied to metal far
more economically and with greater uniformity before the metal is fabricated, that
is while it is still in the coil form, than by any method employed after fabrica-
tion. This means that, by using the coil coating technique, coatings systems can
be applied to metal substrates efficiently and cured precisely so that the ulti-
mate properties of these systems are developed. This yields a coated metal product
of higher quality at a lower cost than can be obtained otherwise.

Today all of us involved in the coil coating industry - the equipment, metal,
pretreatment and coatings suppliers; the coaters and fabricators - have been all
working to bring this concept from the idea stage to a commercial reality. Much
success has already been had, which can be easily appreciated from the coatings
suppliers standpoint by considering that in 1964 some 25 million dollars worth of
coil coatings were purchased. It is estimated that in 1966, 35 to 40 million dol-
lars in coatings will be sold to this industry and there are currently no signs
that the growth curve is going to level off in the foreseeable future.

To satisfactorily accomplish this success and to continue to accelerate this
growth numerous problems had to be solved. The purpose of this paper is to dis-
cuss some of the more universal formulating problems posed by the coil coating
technique, what part vinyls are playing and can play in solving these problems,
and what the suppliers to the vinyl formulator might do to help solve the prob-
lems that are now limiting the use of vinyl in the coil coating industry.

THE COIL COATING TECHNIQUE

Looking at the bare bones of the coil coating process, we see that a coil of

metal is fed into the "coil line" where it is cleaned, pretreated, coated, baked, quenched and recoiled. The coated coil is then transported to equipment where it is slit, sheeted or blanked and then fed into roll forming, break forming or stamping equipment where it is fabricated into the desired part. These parts are then assembled into the end product which is sold to and put into service by the consumer. When developing a coating for coil use it is important that all of these performance areas are taken into consideration and it must be remembered that any compromise made in any of the earlier steps can affect the satisfactory performance of the coated product during assembly and service, and failures at this point generally make the total product unsatisfactory.

With this in mind let us more closely examine the whole process. The first three steps of this process - the choice of metal, cleaning and pretreatment or conversion coating - can be for our purposes lumped together under the term "choice of substrate". To a large extent the ultimate properties of any coil coatings system is determined by the type of substrate chosen. Here we are not only talking about the generic type but also such factors as gauge, alloy, temper, surface smoothness and color are important. Concerning the pretreatment, the quality of pretreatment or conversion coating that can be produced on a coil line is another of the major factors contributing to the overall high quality of prepainted metal products. Pretreatment too not only varies from type to type but also in method of application and amounts of conversion coating applied. As a result of these factors, it is imperative when evaluating a particular coating system for use in the coil coating industry the "substrate" be typical of what is to be used by the coater.

The generic types of substrates most commonly used are aluminum, cold rolled steel and extra smooth hot dipped galvanized steel. Other common types are full spangle hot dipped galvanized steel, electro-galvanized steel and electrolytic tin plate. Common pretreatments for aluminum are Bonderite 721 or Alodine 1200S; for steel, Bonderite #901 or Granodine 1101; and for galvanized steel, Bonderite #1303 or Granodine 92. The pretreated substrate now moves to the application and baking stage. For the sake of simplicity we will consider only single coat systems. The additional complications of a two-coat system will really add very little to this discussion.

By the time we are ready to charge our coating into the coater pan all of the problems I am about to discuss would have already been solved, but for sake of organization, I think it would be of value to point up these problems as we encounter them in processing the coil of metal. One of the disadvantages of this method of presentation is that we will not be discussing these problems in their order of importance. However, it is nearly impossible to talk about the problems encountered in their order of importance because what happens to be of prime importance to one man's operation might not nearly rank as high in another man's operation. Also, it must always be remembered that a successful system is the sum total of a multitude of smaller, sometimes almost insignificant, successes. But, starting at the point where a drum of coating is about to be charged to the coater pan, and assuming that the viscosity stability, resistance to pigment settling, gassing and other aging difficulties have been reasonably adjusted for, the first problem we want to consider is what viscosity range specification should be met to insure satisfactory application characteristics.

The application here is done by a reverse rollcoater. The chief advantage of a reverse rollcoater is that it is capable of applying a wide range of wet film thicknesses smoothly over a wide range of line speeds. The reverse rollcoater applies coatings at a very high rate of shear. This can be of some advantage with materials that are thixotropic in nature and whose structure breaks

down under high shear, but it is a decided disadvantage with materials that have a dilatant characteristic. At high line speeds this very high shear rate produces "chattering" and "skipping" with these types of materials. Without going into a lengthy discussion of rheology, accept the fact that to have satisfactory application properties coatings must meet certain viscosity requirements at these high shear rates available on the coil lines, and so the coaters have fallen back on the traditional Ford cup and Zahn cup type of measuring equipment. These, of course, are low shear instruments and are only of value when the materials which are to be measured are Newtonian, that is that their viscosity properties do not change over a wide range of shear rates. Unfortunately many of the materials which are used on or could be applied by a reverse rollcoater are not Newtonian in nature. This is particularly true of the PVC dispersion type coatings. Although any of the solution type coatings formulated at a high enough non-volatile content exhibit non-Newtonian behavior. This is particularly true of epoxy and thermosetting acrylic types of coatings. The quick answer to this problem is to simply say, formulate low solids coatings. This is unsatisfactory for two reasons. First, one of the biggest advantages of a reverse rollcoater is that it can handle high viscosity materials. This allows great reductions in the amount of solvents used which lowers significantly the coatings applied cost. Secondly, there is an upper limit of wet film thickness that can be adequately handled, and if the volume solids are low it is not always possible to obtain the desired dry film thickness. This leaves as the only practical alternative, the necessity of formulating Newtonian properties into the systems that are to be used on the coil lines, and conducting enough line trials to be certain that these properties are not drastically affected by low temperatures (which I have seen as low as 45°F. but which are generally between 60 and 70°F.) and aging.

Moving to the next step, the coating is charged into the pan and comes under the action of the rolls. Solvent evaporation, and color development are two of the problems I want to discuss under the heading of "machine stability". The ratio of surface area to volume on the pan and rolls of the coater is very high. This makes the rate of solvent evaporation, and its effect on the application and flow properties very important. This is particularly true in the summer time when the the ambient temperature on many lines is 95 to 110°F. In general, this problem is solved by choosing solvents which have low evaporation rates. But, in addition to this, one must be certain that the viscosity/solids relationship for the material in question is such that an increase of 1 or 2% in solids does not drastically increase the viscosity of the system.

Color development can occur because the action of the rolls on a rollcoater, is in many respects quite similar to the shearing action of conventional roller mills used to disperse or grind pigments. So that in instances where pigments are not well wetted by the vehicle, further "grinding" can occur on the rolls. If this pigment wetting variability is a problem inherent in the coating system being used and not corrected for, it makes coil-to-coil color control an extremely tricky business.

Once the coating has been applied, its ability to flow out comes under examination. This is important, particularly in high gloss systems, because there are always some wet film patterns not eliminated by the action of the applicator roll. Flow-out has an opportunity to occur from the time the coating leaves the applicator until the coating is at some point in the oven where all of the solvent has been removed and the coating sets.

Actually, as the coated strip passes through the oven, three things happen. The coating finishes flow-out, solvent is removed, and the coating sets, cures or fuses. Under current practice this is usually allotted 40 to 60 seconds of oven

dwell time. There are, however, some systems on some lines where this dwell time is 15 seconds.

Many of the problems that I have been discussing so far are related to the solvent system and the effect of the solvents on the resin system. "Solvent popping" is another of these types, and occurs either when the film gels before the bulk of the solvent is released, or when low boiling solvent boils instead of evaporating out of the film. Today, this is only a serious problem in thick films (i.e., 1.0 mil or greater) where the resin system has very bad solvent release properties or requires very high temperatures (at the desired line speed) to cure the system such as with some of the thermosetting types that are now available. But, it could also be a problem with dispersion systems of a very high order of molecular weight which also require high fusion temperatures. Here, I am thinking of such resins as polyethylene, polypropylene, or the fluoropolymers.

The two baking problems that I would like to consider now, I put under the headings of "bake sensitivity" or "color sensitivity". What I mean by "bake sensitivity" is that at any given temperature there is a minimum length of dwell time required for a system to develop acceptable physical properties (i.e., color, hardness, adhesion or flexibility); an additional length of time to develop its optimum properties, after which the overall properties begin to fall off. There is then some point in well time reached at which the properties fall below an acceptable limit. This is then the maximum acceptable dwell time. It is the difference between the minimum and maximum acceptable dwell time that I refer to as the "bake sensitivity". The shorter this period of time, the more bake sensitivity the system has. Another way of defining "bake sensitivity" is in terms of substrate or metal temperature where it would be defined as the range of temperature over which acceptable properties were obtained. The latter method has some advantage in that it is a factor independent of oven air temperature. It is also useful in understanding why a coil of metal coated with a material that has a bake sensitivity of only 5 or 10 degrees, often has off-color or poorly fabricated areas a few inches in from each side of the coil edge. It is very difficult to define at what point a material is too bake sensitive to be used on a coil line. Like many of the other problems I am discussing here, compromises can be made for a bake sensitive system if other properties of the system are good enough to warrant them. Another problem connected to bake sensitivity is the quick test for optimum cure. The most popular quick tests used today are pencil hardness, solvent resistance, reverse impact and 180° bend fabrication properties. With many coatings you can simply specify, for example, that if baked on a line to a pencil hardness of F to H, the system has developed its optimum properties and you can be assured that the fabrication and environmental resistance properties (i.e., weathering, corrosion resistance or abrasion resistance) demonstrated by laboratory panels or pilot runs are present in this coil. However, there are many systems particularly some of the newer more sophisticated products which can be shown to have properties far in excess of the older types where meeting even a combination of "quick test" specifications do not guarantee that the desired properties have been developed. About the only thing an applicator can do if he desires to use a system of this type, is to make enough pilot runs and do enough testing so that he can establish line speeds and oven temperatures or metal temperature limitations, and then exercise care that these are maintained on the line when these critical materials are being run. Of course, as anyone who has been associated with production operations knows, the end properties of such a system must be clearly superior to warrant such complications.

After baking, the coated coil is water-quenched and re-coiled. Here, we must be aware of what effect the water will have on the appearance of the coating

(i.e., water spotting) and whether there are any problems caused by the front and back coatings being placed in intimate contact under pressure. The latter problem is generally referred to as blocking, pressure mottling, or gloss mottling. In the more severe cases, the coating or coatings adhere to one another so that when the coil is uncoiled, coating is picked off or transferred from one side to the other. In the less severe, yet still objectionable situations, the gloss of the coating is affected so that there are areas of higher and lower gloss throughout the coil.

Now, if we have had no major failure of the coating system up to this point, we have accomplished the first third of the job, that is, we have produced a satisfactorily coated coil of metal. The next step is the fabrication.

The pitfalls of fabrication are easily as numerous as those of application. This is complicated by the fact that by and large the problems are fairly specific to the operation in question. So, instead of trying to discuss this subject in any detail, let me just mention a few of the considerations that should be made in designing a coating for post-fabrication.

In general, the coils as received from the coating line are slit into narrower widths and then fed into roll-forming, break-forming, stamping, or drawing equipment. The stress and strains placed on the coating substrate system can be studied as the effect of extension, compression and shear forces on the adhesion and flexibility of the coating. Although the various equipment is capable of producing an infinite variety of shapes, it can be shown that all of the operations can be divided into these three distinct categories. For instance, slitting or blanking operations exert primarily compression stresses on the "cut edge". A simple 90° break bend exerts only forces of extension, and in a roll-formed channel all three stresses of extension, compression and shear are generally present. As a result of this observation, it is imperative that when studying the fabrication properties of the coating substrate system we look at the effect of extension, compression and shear on the adhesion and flexibility of the coating, rather than whether or not the coating can be made to pass some arbitrary laboratory fabrication test such as reverse impact, 180° T bends or wedge bends. Now, I am not saying that these laboratory tests cannot be used to evaluate fabrication properties, but that when we use these tests we should use them intelligently, relating them to actual fabrication techniques.

A number of other factors often overlooked are the effect of coil age, the effect of metal temperature, and the effect of external lubricants on the fabrication properties of the system. It is very seldom that a coil is fabricated immediately after coating, usually weeks, and sometimes months pass before the coil is processed. If the coating post hardens or cures on aging, and this is not compensated for at the time of application unsatisfactory results can occur.

Generally speaking, during laboratory evaluation and coil line quality control, the temperature of the panels being evaluated is no lower than 70°F.; however, in production many fabricators seem to find it impracticable to adjust the temperature of the coils and use them at whatever temperature they happen to be, which is often in the neighborhood of 50°F.

Although external lubricants are applied to improve fabrication properties of precoated metal, it is possible that they can adversely affect the adhesion of many systems. This problem occurs primarily with systems which micro-fracture readily on extension. If the lubricant applied to these systems has any penetrating abilities whatsoever, it can be pulled down into the film metal interface and downgrade the adhesion of the system.

Another facet of good fabrication is the ability of a finish to pass through these operations with very little effect to the appearance of the coating. I usually divide these problems into two categories. First, burnishing, mar or scuff resistance, where the coating is hard enough so that it is not physically deformed by the abrasive action of the fabricating equipment. Secondly, die or roll marking resistance. Here, the coating has the property of not picking up a color from contact with the fabricating dies or rolls.

After the fabrication requirements have been met we now are ready to consider the environmental resistance properties. Environmental resistance properties are all those properties which the ultimate consumer expects the finish to possess. Coil coated materials are finiding their way into a wide variety of end use applications, and to discuss any of these in detail would be far beyond the scope of this paper. However, there are a few comments that I would like to make.

Today, 60 to 70% of all coil coated materials go into an exterior building product, such as residential siding, industrial building panels and mobile home construction. As a result of this, the single most desired environmental resistance property is exterior exposure or weathering resistance. In the coil coatings industry when you say a coating has good weathering resistance, it generally means that you have two summers of exposure in subtropical Florida at 45° and that there were no significant amounts of fading or chalking noted on the panel.

Although weathering is important in today's coil coating market, there is still a ten million dollar coatings market for material which do not need excellent weathering properties. Also, keep in mind that the use of coil coated metal is expanding in the automotive and appliance industry and will in the long run over-shadow the present exterior building products.

VINYL COIL COATINGS

To an experienced coatings formulator the application and environmental resistance requirements just discussed are similar to thoseposed by other application techniques. It is the fabrication requirement that sets coil coatings formulations apart from other coating problems.

The first prerequisite for a coating that is designed to withstand fabrication is flexibility. Without flexibility a coating will crack and separate, letting the substrate show through at every point where the substrate has been distorted and hence fail in the coating's primary function of protection and decoration. This will occur regardless of the other good properties such as adhesion, hardness, abrasion resistance, etc.

Of all the resin types commercially available today, vinyl is outstanding for its flexibility. It was for this reason that vinyl modified materials were among the first used in the coil coating industry. However, today, vinyl based coatings hold only 35 to 40% of the market, and is second to the less flexible thermosetting acrylic types of coatings in use. The purpose of this paper is not to compare vinyls with thermosetting acrylics or to attack the acrylics as inferior to vinyls. I only point this fact out so that in the proceeding discussion of vinyl coil coatings attention is given to, and a closer examination is made of, the problem areas of vinyls rather than letting them be easily over-shadowed by their good properties.

The largest single class of vinyl used in the coil coating industry, which I

refer to as "normal vinyls" are coatings formulated using the traditional VYHH/VMCH class of vinyl solution resin. These coatings are characterized by their excellent flexibility, adhesion and film hardness; by their excellent weathering properties, their excellent salt spray, humidity resistance, stain and chemical resistance; by their ability to fabricate after aging and at lower temperatures; and their good rollcoater application and baking properties. Probably the most publicized disadvantage of the normal vinyls is the relatively high applied cost. This high applied cost is due primarily to this type of coating's low volume solids and its need for expensive ketone solvents. Another problem less publicized but nontheless very important, is the poor color and gloss stability of the normal vinyl at the high temperatures that are encountered in the rapid coil coating application technique. Of course, as most people in the vinyl industry know, this color and gloss stability is directly connected with thermal stability problems of vinyl resins, and that these problems have been solved or greatly minimized in unmodified PVC formulations by the development of stabilizer systems. Although these stabilizers are available, practically all of them are rendered fairly ineffective by the presence of carboxyl or hydroxyl containing resins which are generally used as adhesion promoters.

Attempts have been made to lower the applied cost of the normal vinyl type coatings by formulating systems around the newer, lower molecular weight, or more highly soluble vinyl solution resins now available on the market. These systems lower the applied cost primarily by increasing the volume solids of the formulation so that less solvent is required, also lower cost solvents can be used. These are sometimes referred to as "high solids" vinyls. The high solids vinyl system in many cases can be applied with a savings of between 10 and 20 cents per mil per 100 square feet, and are comparable in cost with the termosetting acrylic type systems. Going to the lower molecular weight doesn't help this thermal stability problem any, however, in fact, these systems are more sensitive to baking variation. This reduction in molecular weight also shows up in a slight, but definite reduction in flexibility and exterior exposure resistance. The lower molecular weight also produces a lower softening point which causes these coatings to have greater tendencies to block and pressure mottle. Although these coatings have a definite place in the coil coatings field, if we are looking to improve the overall properties of the normal vinyls by going to the lower molecular weight resins alone, we are moving in the wrong direction.

To move to higher molecular weight vinyl is to suggest the use of the homopolymer of polyvinyl chloride. This, of course, is not used in solution as the lower molecular weight copolymer vinyl resins are, but is used as a fine dispersion of solid resin (PVC) in the organic solvents and plasticizers. These materials are commonly referred to as "plastisols" or "organosols". I define a plastisol as a material based primarily on PVC (85 to 90% of the resin system) and contains no more than 15% of an inactive diluent. Plastisols are generally applied as a two-coat system and at film thicknesses of 3 to 30 mils. There is a small, but significant volume of plastisol being coated in the coil coating industry today for such uses as automobile trim, novelty pattern residential siding, strippable coatings, etc. This volume is sure to grow just as the rest of the industry is growing.

The term organosol I use to describe all the other PVC containing coatings. These high molecular weight vinyl coatings have a number of definite advantages over the normal vinyls or in fact in combination of properties over any other coating currently being used in the coil coating industry. I personally feel that these high molecular weight vinyl based coatings are the ideal material in the full sense of the word, for use on the bulk of all coil coated metal applications. Properly formulated, these coatings have superior weathering qualities,

flexibility, abrasion resistance and as low an applied cost as all, but the lowest cost forming alkyds (65 cents per mil per 100 sq. ft.).

Notice, I did say a properly formulated organosol, and in fact I should also say a properly baked organosol. If you will recall, or better yet, review the requirements of a coating by the coil coating technique discussed in the first part of this paper with the thought in mind that you will be using a material which has a solid resin phase (PVC), a solid pigment phase, some sort of an adhesion promoting, plasticizing and stabilizing system, and a solvent system strong enough to dissolve or compatibilize the adhesion promoter, but balanced so that it does not swell or gel the PVC resin, and is also designed to give good viscosity stability and application qualities to the total system. Remember also, that the organosol must be fully fused and that the dry film must be completely compatible so that the good flexibility and weathering properties of the PVC are fully developed. This, then becomes a very difficult technical problem. Difficult, but not impossible, because there are a number of companies in our industry who have by and large solved these problems and are offering to the coil coating industry the advantages that I outlined above.

As I said before, I am not here to dwell on or sell the advantages of vinyl coatings, but that I want to focus attention on the poorer properties of these materials with the hope that ideas will be generated which will help solve these problems and improve the over-all quality of coating market and expand the use of vinyl in this industry.

As for the formulating problems associated with organosols there are a number which were discovered, sometimes painfully, in the development of the present organosol formulating technology. Most of the following have been solved or at least compensated for in today's formulations.

I should start out by mentioning that the initial problems of viscosity stability and application have been solved and the current organosols present no more problems than the normal vinyls and thermosetting acrylics widely used. Variability in adhesion and weathering results was another problem encountered early in the game and has been generally traced to underbaking of the film which did not completely fuse the PVC to develop the optimum properties of the system.

Formulating a high gloss organosol has been a problem primarily in the past because of the poor pigment wetting properties of PVC resin and the relatively high pigment loadings required to give hiding at the 0.9 to 1.0 mil films being used. Formulating techniques have been developed to expand this gloss range limitation to 90°.

Another problem often brought up when organosols are discussed in the poor die or roll marking resistance and burnishing resistance of these materials at very low gloss ranges. The general problem of roll marking and burnishing of low gloss materials has not been solved as such, but modifications have been made to bring organosols up to the point of being equal to anything else on the market.

One problem in which little progress has been made is in this area of gloss and color stability. Although the organosol is generally superior to the normal vinyls in thermal stability, further improvements would certainly be welcome. The problem here is the same with the solution vinyl types that the presently available stabilizing material are not sufficiently effective in the presence of the current adhesion promoting systems. I can see three ways of attacking this problem:

1. Design a PVC resin with improved thermal stability characteristics.

2. Design a stabilizer system which is effective in the presence of hydroxyl or carboxyl containing adhesion promoters.

3. Design an adhesion promoting system for PVC which does not degrade the present commercially available stabilizers.

The last suggestion, that is the design of an improved adhesion promoting system, is also something of general interest. Actually, a good compatible, novel adhesion promoting system could really do a lot to increase the use of the organosol system.

In closing, let me say that the coil coating market is expanding at a rapid pace and its future is a very healthy one, and vinyl is still the best coating choice when all of the requirements are taken into consideration. There are formulating problems, and it is easy to make a poor vinyl; many inexperienced paint companies have. But, when properly formulated, the vinyl coating will give more of what is expected of a good coil coating than anything yet devised. There is room for improvement as there is with any good thing, and I hope that some of my comments made here will initiate some ideas which will lead to these improvements.

ADDITIVES FOR IMPROVING ADHESION OF POLYVINYL CHLORIDE DISPERSIONS

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INTRODUCTION AND BACKGROUND

With the aid of new high speed, automated machines, the precoating of metal is one of the fastest growing segments of the coatings industry.[1] Experiencing a growth rate of 15-20% per year, coil coating is expected to increase from 2.6 billion square feet in 1963 to 8-10 billion square feet by 1973.

Polyvinyl chloride (PVC) systems have been of interest as coatings for many years due to their outstanding chemical resistance, inherent toughness and flexibility. One source estimates that 35-40% of precoaters' resin purchases are vinyls.[2] Acceptance of organosols as one type of vinyl finish by metal coil coaters indicates that organosols, too, will account for an ever-increasing share in the metal finishing market in the future. Another indication of the rapid growth of vinyl-coated metals is the estimated 200 million square feet of metal which will be vinyl clad in 1970. That amount is four times the 1965 estimated figure of 50 million and almost eight times the 27 million square feet reported in 1963.[3]

PVC dispersions are gaining importance in coatings with the introduction of improved formulating techniques, newly developed additives and more sophisticated resins. For example, variations are possible which can give PVC coatings with hardness values ranging from a hard, tough film to a soft, resilient foam sheet. Also, a film may be applied to give either a permanent "lifetime" coating or only temporary protection as with a peelable film.

Vinyl copolymer, solution-grade resins are commonly used as coating materials. These air-dryable systems are widely accepted coatings because of their excellent chemical resistance and durability.

Simple, heat-fused PVC plastisol formulations containing a stir-in resin, plasticizer, stabilizer and pigment also can be used as coating materials. Volatile diluents, such as aliphatic or aromatic hydrocarbons, are often added to these systems to form organosols for ease of handling and application. When solution resin coatings are compared with PVC organosol coatings, the organosols have advantages of a higher solids content and the use of low-cost solvents. With organosols, a thicker coating may be deposited in one pass to produce a tough film.

Specific formulations for organosol metal finishes depend on the actual method of application, the type of metal surface to be coated, and the end-use application of the coated metal. When used with a good primer, vinyl organosol

coatings may be applied as finishes to metal sheet and coil without fear of loss of adhesion, flaking or cracking during subsequent metal-forming operations. The unusual formability of these coatings, even after aging, is an outstanding characteristic. Generally metal coated with PVC organosol systems can be made to withstand severe fabricating operations, including cutting, bending, perforating, punching, stamping and roll forming.

However, the adhesion of ordinary plastisols and organosols to various substrates, especially metals, is deficient and must be aided in some way to provide an acceptable coating. Various techniques are used to improve the adhesion of vinyl dispersions. A broad classification would divide these techniques into two main types - first, those vinyl coatings requiring a primer coat to be applied prior to the vinyl coating; and second, those coatings depending upon an internal modification. In order to establish a proper perspective, each type should be considered separately.

A. Primers[4]

   1. Vinyl copolymer resins

      One of the earliest types of primers developed, based on certain vinyl copolymers, was found to improve coating adhesion to substrates, particularly when applied as solution vinyls. Stability has been a problem with these materials and careful control of the cure cycle is critical.

   2. Acrylic resins

      Probably the most widely used commercial primers available today are the acrylic resins of both the thermoplastic and thermosetting types. These resins find use in primer formulations for several reasons, including excellent specific adhesion, extreme resistance to plasticizer migration, resistance to the solvent action of the plasticizer during fusion of the plastisol, and compatibility with the vinyl resin.

   3. Phenolic, epoxy and polyester resins

      This class of polymers contributes good to exceptional adhesion to a wide range of substrates. Generally, they contribute greatly to the chemical-, solvent-, and immersion-resistant properties of primers in which they are components. A primer from this group, however, must be selected carefully because of the differences in properties exhibited by the individual resins. Shortcomings of this group, particularly of the phenolics, include lack of flexibility and poor impact strength.

   4. Urethane polymers

      Among the newer materials being evaluated for plastisol and organosol primers are the urethanes. These materials exhibit outstanding adhesion and have excellent resistance to high temperature. Indications are that excellent primers may be formulated from the urethanes.

The use of a primer coat offers two disadvantages. First, the coating process is a two-coat operation, requiring more time and equipment than that

required in the single-coat operation. Secondly, if a thermoplastic primer (i.e., a vinyl copolymer primer) is used, it must be air or force-dried to remove the volatile solvents. The problem is somewhat complicated when a thermosetting primer (i.e., a heat-reactive phenolic resin) is used, which must be heated sufficiently for a reaction to take place. Most thermosetting resins have a critical curing cycle and are subject to being undercured or overcured. Also, the dark color of some of these resins severely limits the use of these primers.

There is no single primer formulation suitable for every application. Careful analysis of all the desired characteristics must be made before deciding upon the proper formulation.

B. Plastisol Modification

A second approach to attaining plastisol adhesion is modification of the plastisol so it will become self-adhering. This modification can be accomplished in various ways.

1. Vinyl copolymer resins

A vinyl copolymer resin can be used as a partial replacement for the dispersion-grade PVC resin. Certain of these resins, such as the maleated polyvinyl chloride-polyvinyl acetate copolymer resins, have particularly good adhesion when used as a primary resin in a coating system. As previously mentioned, these resins often are used as primers for PVC dispersion systems. If carefully blended into a dispersion in adequate amounts, however, the resin will lend some of its adhering qualities to the coating without destroying all of the other inherent qualities of the dispersion system itself.

One advantage of using a system that gives a one-step organosol coating process is the heavy coating thicknesses that are possible in one pass. A higher solids content may generally be obtained with dispersion resins than when the solution vinyl is used as the sole resin. A frequent disadvantage to the use of a mixed dispersion-solution resins system is the inability to obtain the adhesion and abrasion resistance normally possible with a good PVC dispersion system used over a good primer undercoat. Problems also may be encountered with viscosity stability.

2. Reactive Materials

Adhesion may be aided by inclusion in the plastisol of monomers which cross-link or polymerize as the vinyl is fused. Diallyl phthalate has been evaluated extensively in this application and with careful formulation and control can be effective.[5,6] Triallyl cyanurate also can be used and is reported to bond well in a plastisol coating on phosphatized steel of alodized aluminum.[7] Epoxies, phenolics and other reactive materials are also used as modifiers to aid adhesion.

Problems that arise, particularly in thick films, in the use of a reaction mechanism to gain adhesion include the shrinkage of the coating when cooled and the heat given off by the reaction, if it is exothermic. The shrinkage of some reactive materials can be sufficient to destroy any adhesive bond caused by the reaction. Heat buildup by a high exotherm can cause film and bond degradation problems. To solve these difficulties often calls for careful selection of amounts and types of reactive ingredients, and frequently, extreme care must be exercised during fusion.

Considerable work has been performed in our laboratories on plastisol modification with specialty plasticizers which aid the adhesion of dispersions. These materials, which have been called "plasticizer-adhesives", act both as aids to adhesion and as PVC plasticizers. Upon close examination, these materials offer unusual properties and characteristics which can be useful for many coatings operations. In many applications, a one-coat finish may prove acceptable where two or more coats were previously required.

PLASTICIZER-ADHESIVES

To date, the studies of the plasticizer-adhesives have mainly involved three different products. The first product of this series was designated in laboratory and plant evaluations as Plasticizer-adhesive 80-2.* As a plasticizer, its effect was found to resemble that of some high-molecular-weight polymerics, offering good extraction resistance and being about 50% as effective as di-(2-ethylhexyl) phthalate (DOP) for producing softness and flexibility. Being a viscous liquid, it could be incorporated into a PVC dispersion coating system by conventional techniques. Plasticizer-adhesive 80-2 (Pz-ad 80-2) was found to be an effective aid to adhesion in thin film applications where toughness and chemical resistance were important. Because of its high viscosity, it appeared particularly useful for organosols in which film softness was not necessarily desired.

Plasticizer-adhesive 80-6** is a monomeric-type material having a much lower viscosity than does Pz-ad 80-2. Its properties were found to be particularly useful in applications where this lower viscosity is considered important. Upon comparison of the two compounds, Pz-ad 80-6 showed less effectiveness for promoting adhesion, but produced more plasticizing action at equal concentrations. Equivalent adhesion could be attained with either of these two products with the use of 50-60% more Pz-ad 80-6 than Pz-ad 80-2 in the formulation. Although coatings containing Pz-ad 80-6 appeared much more flexible, unusual surface hardening occurred during fusion giving a PVC film with good toughness and abrasion resistance.

Pz-ad 80-2 and Pz-ad 80-6 were most effective for thin film applications. When a heavy PVC coating containing these materials was applied, adhesion was found to decrease as the film thickness increased. For heavy PVC dispersion coatings of over 20 mils (0.5mm.), another plasticizer-adhesive, Pz-ad 90-4**, was found to be quite effective.

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* Marketed as KODAFLEX AD-2. KODAFLEX is a trademark of Eastman Kodak Co.
**Developmental product at present.

The effects of the plasticizer-adhesives on the adhesion of plastisol coatings at various coating thicknesses are illustrated in Figure 1. The compositions of these plastisols are noted in Table I; coating adhesion was evaluated by determinations of peel strength. In certain cases, plastisol modification with the plasticizer-adhesives resulted in peel strengths great enough to cause coating rupture rather than bond failure during testing. Most PVC dispersion coatings applied at film thicknesses less than 2-3 mils (0.05-0.08 mm.) ruptured when the peel strength exceeded 8-10 pounds per inch (1.4-1.8 kg./cm.). Similarly, many fused plastisols were found to tear and break rather than peel when the peel strength of a 20-mil (0.51 mm.) coating exceeded 20 pounds per inch (3.6 kg./cm.).

A. Formulating Characteristics of Plasticizer-Adhesives

Several commercial, general-purpose, dispersion-grade PVC resins, when modified with the plasticizer-adhesives, produced coatings with satisfactory adhesion. However, some resins did give slightly better adhesion than did others. The soap content of a resin appeared to affect the coating adhesion; those resins lowest in soap content showed the best adhesion. The choice of a resin should depend primarily on the end application of the coating with fusion conditions, viscosity and film appearance being important factors.

The plasticizer-adhesives were found to perform satisfactorily in combination with other conventional PVC plasticizers, when evaluated for their influence on adhesion. For example, the concentration of plasticizers could be adjusted to yield any film softness and flexibility desired. Adhesion was found to be just as great with softer films as with harder films, although the plasticizer-adhesive concentration often had to be adjusted in order to keep the relative per cent concentration constant.

Certain stabilizers were found to cancel the adhesion-promoting properties of these additives. The general PVC stabilizers containing barium, cadmium and zinc soaps plus a metal chelator generally could not be used. The metal chelator was particularly could not be used. The metal chelator was particularly effective in destroying the adhesive effects of Pz-ad 90-4. However, other stabilizers for PVC such as certain tin compounds, dibutyltin maleate for example, and commonly used epoxies such as epoxidized soybean oil had no adverse effects on adhesion.

The plasticizer-adhesives also performed satsifactorily in dispersion coatings containing pigments and fillers. These additives had no significant effects on the adhesion-promoting properties if the concentration of plasticizer-adhesive was adjusted to overcome any dilution effects caused by addition of large amounts of these additives.

In typical organosols, the plasticizer-adhesives were found to be compatible with all the components except the aliphatic hydrocarbon diluents. However, these diluents could be used if blended with appropriate aromatic hydrocarbons. Generally, a 25-50% concentration of aromatic diluent was required in a hydrocarbon diluent system to achieve proper compatibility. The total concentration of volatile diluent could be adjusted to meet application requirements. It has been found that organosols of 55-80% solids could be sprayed

onto substrates such as cold-rolled or phosphatized steel, alodized or anodized aluminum to produce coatings of around one mil (0.025 mm.) thickness with excellent adhesion.

Vinyl foams were also found to adhere to substrates when the foams were modified with the plasticizer-adhesive. The addition of Pz-ad 80-2 or Pz-ad 80-6 to a typical plastisol containing a small amount of azobisformamide was found to increase this adhesion to the point where the foam would tear rather than peel from the substrate.

B. Performance of Plasticizer-Adhesives in Plastisols

The effect of film thickness on the adhesion of plastisols containing the plasticizer-adhesives was shown in Figure 1. These typical plastisols were formulated for maximum adhesion. Actually, by varying the concentration of a plasticizer-adhesive while maintaining the concentration of the other ingredients at a constant level, adhesion can be controlled over a fairly wide range.

Figure 2 illustrates the differences in adhesive strength resulting from varying the concentration of Pz-ad 80-2 or Pz-ad 80-6 in a typical soft plastisol coating. Peel strength was used as an indication of adhesion. In this example, coating adhesion to unprimed, cold-rolled steel was found to be adjustable from less than one-fourth to approximately ten pounds per inch (0.045 to 1.799 kg./cm.) peel strength, the latter resulting in film rupture on testing. Adhesion of this plastisol coating to polished aluminum and abraded or sanded aluminum also was increased, but to a lesser degree.

Figure 3 shows the variation of peel strength or degree of adhesion of a plastisol coating as the concentration of Pz-ad 90-4 is increased. The hardness of the coating was maintained constant over the range of the test by adjustments in the concentrations of the other plasticizers, DOP and TMPD diisobutyrate.

As indicated, Pz-ad 90-4 produced maximum adhesion, over 20 pounds per inch (3.6 kg./cm.), at 40-50 phr. Adhesion of 20 ppi. (3.6 kg./cm.) or greater at the slow peel rate of two inches (5.1 cm.) per minute is more than adequate for most applications and usually coating rupture occurs before bond failure.

This ability to adjust the adhesive properties of a PVC coating by varying the concentration of the plasticizer-adhesives makes possible plastisol applications where complete coating ahdesion is unnecessary or, in many cases, undesirable. One such application is strippable coatings for materials which will be processed, post-formed, or subjected to unusually severe handling between application and removal of the coating.

C. Effect on General Coating Properties

The preceding discussion focused primarily on the adhesion properties of PVC plastisol coatings containing the plasticizer-adhesives. These materials may also affect other properties of the coatings as indicated by the data in Table II. The formulations were selected to yield soft films of equal hardness (Shore A Durometer hardness of 70). One noteworthy factor shown by this data was the high resistance

of the plasticizer-adhesives to oil and heptane extraction. In special finishes this feature could be enhanced further by the use, with the plasticizer-adhesives, of plasticizers having equal resistance to extraction.

D. Performance of Plasticizer-Adhesives in Organosols

As previously mentioned, Pz-ad 80-2 and Pz-ad 80-6 have been found to be particularly effective in promoting adhesion in thin film or-fanosol coatings. In this application, Pz-ad 90-4 offered no improvement over these first two plasticizer-adhesives. A typical formulation exemplifying the use of Pz-ad 80-6 for a thin organosol coating is given in Table III.

This formulation could be sprayed onto cold-rolled or phosphatized steel or onto alodized or anodized aluminum at 55-65% solids in hydrocarbon diluents to give a one-mil (0.0254 mm.) dry film thickness. When fused on any of these substrates using a graduated fusion cycle of 2-4 minutes at 350°F. (177°C.) and 1-2 minutes at 450°F. (232°C.), the coating was found to pass the following tests:

1. Reverse Impact, 100 inch-pounds (94 cm.-kg.) - No film rupture or notable loss of adhesion.

2. One "T" Bend - No film rupture or notable loss of adhesion.

3. Tape Adhesion Tests - No film removal upon testing before and after remaining under water for 24 hours at 73°F. (23 C.).

More severe testing on this type of coating is still being conducted. Differences in coating adhesion were noted on different substrates, of course. The best adhesion has been obtained on cleaned, cold-rolled steel but adhesion to phosphatized steel and to anodized or alodized aluminum has also been found satisfactory for many applications.

WEATHERING PROPERTIES OF MODIFIED PVC COATINGS

The addition of Pz-ad 80-2 did not appear to have any adverse effects on the weathering characteristics of pigmented or filled PVC dispersions. As shown in Table IV, the plasticizer-adhesive had little, if any, effect on the color change of a clear PVC dispersion coating during accelerated weathering tests. Six-months' outdoor weathering exposure indicated a similar trend in color change.

Salt spray tests have shown that PVC dispersions incorporating Pz-ad 80-2 are promising as surface coatings for bonderized steel. These dispersions have also given good results on other types of steel surfaces when the substrate was completely encapsulated by the coating. In contrast, significant undercreep occurred when PVC surface coatings containing Pz-ad 80-2 were applied to cold-folled steel panels and cross-hatched before prolonged exposure in salt spray.

Although PVC coatings containing Pz-ad 80-6 and Pz-ad 90-4 have not been tested for weathering resistance as extensively as have coatings containing Pz-ad 80-2, indications are that similar results should be expected. As can be noted

in Table IV, unpigmented (clear) vinyl did not weather well when in direct contact with steel. However, the pigmented vinyl weathered very well and should perform satisfactorily during outdoor exposure in many applications. Generally, the inclusion of plasticizer-adhesives did not change the weathering characteristics of ordinary plasticized vinyl.

SUMMARY

The results of this study have shown that PVC dispersions now can be used effectively as one-coat finishes, especially for certain metal substrates. These one-coat systems should be able to compete effectively for many present applications and open many new-use opportunities for tough, abrasion-resistant, chemical-resistant coatings that are flexible enough for severe post-forming operations.

Plasticizer-adhesives are an interesting approach for solving both the adhesion and flexibility requirements for dispersion coatings. Being compatible with ordinary PVC dispersions, the plasticizer-adhesives could be used in these formulations to give a wide range of protective finishes. These finishes could be one-component systems with good clarity, improved color stability and longer shelf-life. Also, conventional fusion techniques for PVC dispersions were found to work well when using the plasticizer-adhesives. Their performance as plasticizers, as well as aids to adhesion, were found to be acceptable in PVC dispersion coatings and finishes for many interior and exterior applications.

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TABLE I

TYPICAL PLASTISOL FORMULATIONS[a] USED IN COMPARISONS OF COATING ADHESION

Ingredients	PHR[d]			
	A	B	C	D
PVC dispersion resin	100	100	100	100
Pz-ad 80-2	50	-	-	-
Pz-ad 90-4	-	50	-	-
Pz-ad 80-6	-	-	80	-
DOP[b]	20	20	5	45
TMPD diisobutyrate[c]	25	25	10	25
Dibutyltin maleate	1	1	1	1
Epoxidized soybean oil	5	5	5	5

[a]PVC films were coated on untreated, cold-rolled steel and fused for four minutes at 190-200 C. in a forced draft oven. The peel strengths were determined by peeling a one-inch (2.54 cm.) strip of coating from the substrate at a rate of two inches (5.1 cm.) per minute and an angle of 180° to the substrate. An Instron Universal Testing Instrument was used to determine the peel strength value in pounds per inch (kg./cm.) of width.

[b]Di-(2-ethylhexyl) phthalate.

[c]2,2,4-Trimethyl-1,3-pentanediol diisobutyrate, marketed as KODAFLEX TXIB.

[d]Parts per hundred parts of resin.

TABLE II

PROPERTIES OF TYPICAL PVC PLASTISOLS MODIFIED WITH PLASTICIZER ADHESIVES

Formulation:[a]		PHR			
		A	B	C	D
PVC dispersion resin		100	100	100	100
Dibutyltin maleate		1	1	1	1
Epoxidized soybean oil		5	5	5	5
Dioctyl phthalate		20	7	20	45
TMPD diisobutyrate		25	7	25	25
Pz-ad 80-2		50	-	-	-
Pz-ad 90-4		-	-	55	-
Pz-ad 80-6		-	80	-	-

Properties	ASTM Method	A	B	C	D
Tensile strength, psi	D638	1700	1750	1800	1850
kg./cm.^{2}		120	123	127	130
100% Modulus, psi	D638	700	730	720	750
kg./cm.^{2}		49.2	51.3	50.6	52.7
Ultimate elongation, %	D638	350	390	420	400
Tear resistance, ppi	D1004	400	350	300	200
kg./cm.		71.6	62.6	53.7	35.8
Shore "A" Durometer hardness, 5 sec.	D1706	70	70	70	70
Extraction properties, wt. % loss					
Soapy water (1% soln.)	D1239	0.5	1.2	1.0	1.3
Oil		0.2	1.0	2.5	9.3
Heptane		16	9	16	26
Activated carbon extraction:	D1203				
Loss, %		3.9	4.1	3.9	5.3
Thickness, mils		10	10	10	10
mm.		0.25	0.25	0.25	0.25
Torsion modulus, °C.	D1043				
35,000 psi		-38	-39	-34	-47
135,000 psi		-60	< -60	-59	< -60
Viscosity,[b] poises after					
aging for: 1 day		42	15	30	18
7 days		70	17	36	18
14 days		79	18	36	19
21 days		79	18	36	19

[a]Sample Preparation: Plasticizers and stabilizers were added to the resin in a Hobart mixer operating at its slowest speed. When the resin became "wet", plasticizer addition was interrupted and the mixture was stirred for approx. 10 min. at this high viscosity state to obtain good dispersion. Then, the remaining plasticizer was added slowly with agitation to obtain maximum plasticizer dispersion as the viscosity of the mixture decreased. The plastisols were then placed under vacuum to remove entrapped air.

The plastisols were cast on glass plates to yield fused films of approx. 10 mils (0.127 mm.) thickness. The films were cured at 350°F. (177°C.) for 5 min.

[b]Brookfield, No. 4 spindle, 6 rpm, 23°C.

TABLE III

TYPICAL ORGANOSOL FORMULATION CONTAINING PLASTICIZER-ADHESIVE

Composition	Parts by weight
PVC dispersion resin	100 parts
Pz-ad 80-6	90 PHR
Polymeric plasticizer 864	10 PHR
Dibutyl tin maleate	1.5 PHR
Epoxidized soybean oil	10 PHR
Titanium dioxide pigment	15 PHR
Calcium carbonate filler	25 PHR
Color-pigment	5 PHR
Aliphatic and aromatic hydrocarbon diluents	To desired viscosity

TABLE IV

EFFECT OF PZ–AD 80–2 ON WEATHERING RESISTANCE OF PVC COATINGS

Formulation:[a]	PHR A	B	C	D
PVC dispersion resin	100	100	100	100
Dibutyltin maleate	1	1	1	1
Epoxidized soybean oil	5	5	5	5
Dioctyl phthalate	20	5	5	45
TMPD diisobutyrate	25	25	25	25
Pz–ad 80–2	50	50	50	–
Titanium dioxide pigment	–	30	20	–
CaCo$_3$ filler	–	–	20	–

Substrate:	Hours of Exposure[b]	Condition After Exposure[c]			
Aluminum[d]	200	1	1	1	1
5–mil (0.127–mm.) coating	400	3	1	1	1
	600	5	1	1	3
Glass	200	1	1	1	1
5–mil (0.127–mm.) coating	400	3	1	1	3
	600	5	1	1	4
Steel, phosphatized[e]	200	1	1	1	1
5–mil (0.127–mm.) coating	400	3	1	1	3
	600	5	1	1	4
Steel, cold–rolled[f]	200	3	1	1	1
10–mil (0.254–mm.) coating	400	4	1	1	2
	600	4	1	1	5
Steel, primed[g]	200	1	1	1	1
10–mil (0.254–mm.) coating	400	2	1	1	1
	600	3	1	1	2
Steel, cold–rolled[h]	200	1	1	1	1
encapsulated, 20–mil	400	2	1	1	1
(0.508–mm.) coating	600	3	1	1	2

[a]See Table II for method of preparation.

[b]Hours exposed in Atlas Weather–Ometer.

[c]Panels rated visually as follows:
  1 = No color change
  2 = Light yellow
  3 = Yellow
  4 = Amber
  5 = Black

[d]Alclad 2024T3 aluminum panels.

[e]Phosphatized cold–rolled steel.

[f]S–39 Q–panels, ground steel.

[g]S–39 panels primed with B. F. Goodrich A1104 B primer

[h]Dip–coated S–39 panels.

Peel Strength

Ppi.	Kg./Cm.
10	1.790
8	1.432
6	1.074
4	0.716
2	0.358

Film Ruptured

Substrate:
A – Cold-rolled steel
B – Abraded aluminum
C – Polished aluminum

Pz-ad 80-2
Pz-ad 80-6

Plasticizer-Adhesive Concn., PHR

[a]Formulation:

PVC dispersion resin	100 parts by wt.
Dibutyltin maleate	1 phr
Epoxidized soybean oil	5 phr
Dioctyl phthalate	20 phr
TMPD diisobutyrate	25 phr
Plasticizer-adhesive	As shown

Coating applied to obtain dry film thickness of 5-mils (0.127-mm.).

FIGURE 2: Effect of Plasticizer-Adhesive Concentration on Adhesion of Plastisol Film[a]

FIGURE 3: Effect of Pz-Ad 90-4 on Peel Strength of Plastisol Coating

Peel Strength

Kg./Cm.	Ppi.
4.47	25
3.58	20
2.68	15
1.79	10
0.89	5

Plastisol B

Plastisols A and C

Plastisol D

Film Thickness

Mils / Mm.: 5 / 0.13, 10 / 0.25, 15 / 0.38, 20 / 0.51, 25 / 0.64, 30 / 0.76, 35 / 0.89, 40 / 1.02, 75 / 1.91, 150 / 3.81
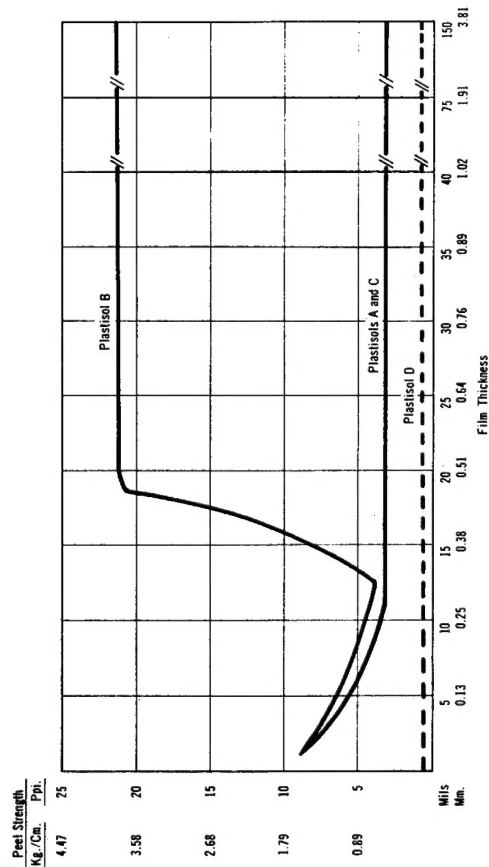
FIGURE 1: Effect of Plasticizer-Adhesives on Film Adhesion of Typical PVC Plastisols (Plastisol Compositions in Table I)

Peel Strength
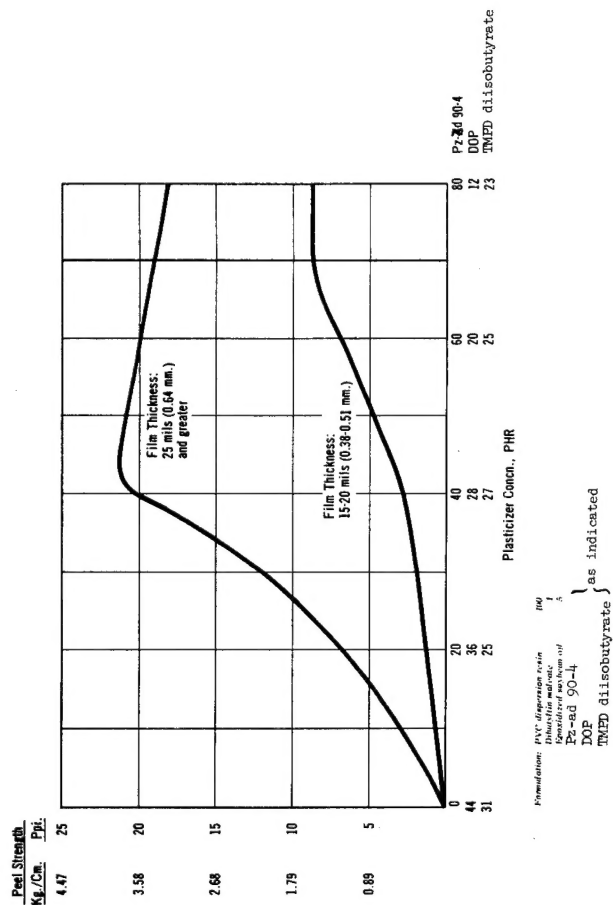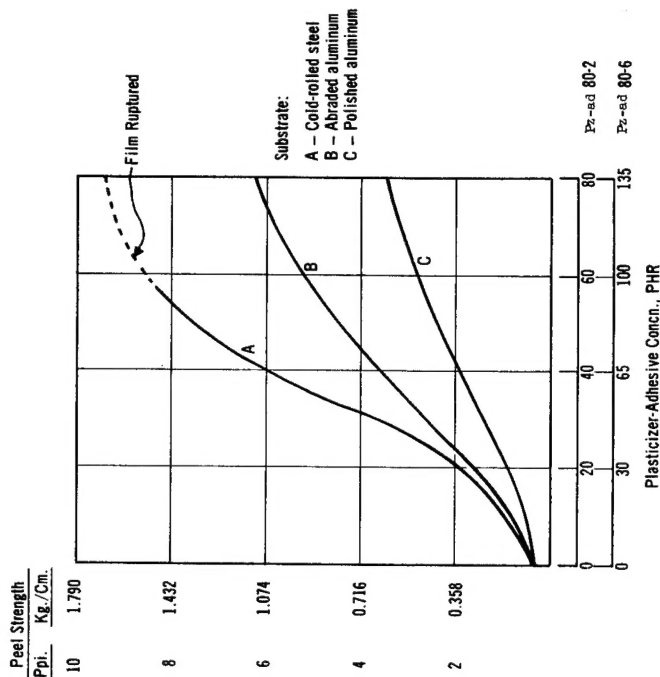
Kg./Cm.	Ppi.
4.47	25
3.58	20
2.68	15
1.79	10
0.89	5

Film Thickness:
25 mils (0.64 mm.) and greater

Film Thickness:
15-20 mils (0.38-0.51 mm.)

Plasticizer Concn., PHR

Pz-Ad 90-4	20	40	60	80
DOP	36	28	20	12
TMPD diisobutyrate	25	27	25	23

44
31

Formulation: PVC dispersion resin 100; Dibutyltin maleate 1; Epoxidized soybean oil 5; Pz-ad 90-4 / DOP / TMPD diisobutyrate as indicated

<table>
<tr><td>

INITIATION FEE

MUST BE ATTACHED

FOR PROCESSING.

</td><td>

SOCIETY OF PLASTICS ENGINEERS, INC.

65 Prospect Street, Stamford, Conn. 06902

348-7528 AREA CODE 203

MEMBERSHIP APPLICATION

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Executive Office Use Only

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</table>

I hereby make application for { ☐ admission into / ☐ reclassification within / ☐ reinstatement in } the Society of Plastics Engineers, Inc. in the grade of membership indicated below for which I believe I am qualified. (See instructions on reverse side.)

Grade	Initiation Fees	Annual Dues	Foreign Dues
☐ Senior Member	$10.00	$20.00	$17.50
☐ Member	10.00	20.00	17.50
☐ Affiliate Member	10.00	20.00	17.50
☐ Student Member	None	5.00	5.00

I wish to affiliate with the _____

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(Geographical location. See listing on reverse side.)

Applicants Full Name _____
    (First)   (M.I.)   (Last)   (Citizen of)   (Birthdate)

Please fill in both addresses and **CHECK THE ONE TO WHICH YOUR MAIL SHOULD BE ADDRESSED.**

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    Position _____

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☐ **HOME:** Address _____ City _____ State _____ Zip Code _____

REFERENCES   The By-Laws require the names of three references who are familiar with your work. One of them should be a member of the Society. Assistance in providing member-references, when needed, will be given on request.

1. _____ Address _____

2. _____ Address _____

3. _____ Address _____

STATEMENT OF COLLEGE WORK

Years Attended From	Years Attended To	Institution	Major and Minor	Degree	Experience Credits See reverse side
				Total Education Experience Credits	

RECORD OF QUALIFYING EXPERIENCE IN PLASTICS

Dates From Mo.	Yr.	To Mo.	Yr.	Give your title, name and location of employer, and name of immediate superior for each position. List in chronological order. Describe duties fully and state briefly any important engineering work you have done in in each position. If space is not sufficient, use a separate sheet.	Time in years and months

I certify that the statements made in this application are correct. I agree, if elected, to be governed by the Constitution and By-Laws of the Society, and to promote the objective of the Society.

Total qualifying years of experience.

Total education and qualifying experience credits.

CREDENTIALS COMMITTEE USE ONLY

Approved (Signature) _____ Date _____

Approved (Signature) _____ Date _____

_____   _____
Date of Application   Signature in ink.

MEMBERSHIP APPLICATION

SOCIETY OF PLASTICS ENGINEERS, INC.

65 Prospect Street, Stamford, Conn. 06902
348-7528 AREA CODE 203

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COMPLETING THE APPLICATION

Grade of Membership

Membership grades are based on experience credits which are earned as follows:

1. Experience credits earned for education.

Doctorate in science or engineering subject:	**6 credits**
Masters in science or engineering subject:	**5 credits**
Bachelors in science or engineering subject:	**4 credits**
Other degree in non-science or non-engineering subject:	**2 credits**

Maximum credits allowable for education shall be six (6).

When filling in the "Statement of College Work" on the reverse side of this application, please place the corresponding number of credits earned in the right-hand column.

2. Experience credits for qualifying experience in plastics or plastics engineering are earned at the rate of one (1) per year, e.g. 5½ years of qualifying experience = 5½ credits. *Please detail carefully the engineering skill required for each position to help the Credentials Committee judge experience as "qualifying."*

When filling in the "Record of Qualifying Experience in Plastics" on the reverse side, please place the amount of time spent in each position (in years and months) in the right-hand column.

When you have determined the number of credits which you believe you have earned consult the following membership grade requirements. Indicate on the reverse side the grade of membership for which you believe you are qualified.

GRADE	REQUIREMENTS
Senior Member	Minimum of twelve (12) experience credits and maintained continuous membership in the Society for a minimum of two (2) years.
Member	Minimum of six (6) experience credits.
Affiliate Member	Less than six (6) experience credits
Student Member	Regularly enrolled student (full- or part-time) in a course of study in plastics and between the ages of 16 years and 26 years, inclusive.